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RESEARCH ON COLOUR PHYSICS AT SOUTH KENSINGTON, 1877–1942

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ABSTRACT. The colour research carried out by Sir William Abney at South Kensington is briefly reviewed and compared with that carried out more recently in the Technical Optics Department of the Imperial College. The instrumental methods employed by Abney and the writer are examined in relation to current problems in the design of colorimeters and spectrophotometers, including mechanical construction, viewing of the matching field, intensity control, and precision of the optical parts. The spectral-mixture curves measured at the College are discussed in connection with the variation of colour matching amongst different observers and with the possibility of correcting these variations. The work on colour discrimination is reviewed, and its bearing on the specification of colour tolerances and the derivation of a uniform-chromaticity scale discussed. Suggestions are put forward for future research on colour physics.

§ 1. INTRODUCTION

IT must be rare that almost continuous research on one subject at one place has been maintained for so long a period as 65 years, yet it was in 1877 that Sir William Abney first entered the Science and Art Department at South Kensington. After only a few months' residence there, Abney established a laboratory in a hideous iron building which, with its companions, became known as the "Brompton Boilers". Ultimately, when various colleges were incorporated in one organization, namely, the Imperial College of Science and Technology, Abney acquired excellent laboratory facilities in the new building of the Royal College of Science, but this was not until thirty years later, in 1907. A great deal of Abney's work was on photography, and it was through photography that his interest in the spectrum and in colour vision was aroused. He continued active experimental work up to the outbreak of the last war, having carried out pioneer researches on colour vision and colour measurement.

It is a remarkable fact that not only has colour research been continuous for 65 years, but some of the problems that have been tackled in the last few years are almost identical with those investigated by Abney. The main hope that we have of finding solutions where Abney failed lies in the fact that in the intervening years many misconceptions about colour have been removed, a great deal more has been learned about the physiological processes of vision, and the

technical equipment available to workers in photometry and allied subjects has been vastly improved.

In his later days, Abney was assisted in much of his work by Professor W. Watson, but little was done on colour during the last war until the Technical Optics Department was formed in 1917. Abney's colour-patch apparatus was then included as part of the equipment of that department, and research and instruction were continued by Professor L. C. Martin and others. In 1926 the Medical Research Council, through the kindly influence of Sir John Parsons, became the fairy godmother of colour research at the College, and they have held that office ever since. I should like to take this opportunity of publicly acknowledging our very real indebtedness to them for the most generous help we have received and for the complete freedom we have been given to develop research along the lines that appeared to us to be most profitable.

A programme of work was prepared by Professor Martin and Professor H. Hartridge, the first problem tackled in 1926 being the re-determination of the spectral-mixture curves, information that was, as reported by Mr. Guild at the Optical Convention in 1926, urgently needed for colorimetric purposes and was also of very considerable physiological interest. I was invited to undertake this investigation under the supervision of Professor Martin, and I have a further debt to acknowledge for the help and support which Professor Martin has always given me, and again for freedom in developing the research. My first task was to design a new trichromatic colorimeter, and I was fortunate enough to adopt a general arrangement that was found subsequently to lend itself to many different types of observation beyond the original problem of the colour-mixture curves. Research with that apparatus has been in progress continuously since 1926, although I have not myself been at South Kensington during the whole of that period.

So much for a brief historical outline of the activities here from 1877 to 1942. I propose now to deal with some of the salient points of the actual investigations and their impact on current problems in colorimetry, and to contrast the methods adopted by Abney with those used more recently in the Technical Optics Department.

§ 2. INSTRUMENTAL ARRANGEMENTS

Abney's colour-patch apparatus is too well known to require detailed description here, and those who wish for more information can readily obtain it from Abney's original reports (Abney, 1913). Similarly, I do not wish to spend time on the details of my own colorimeter (Wright, 1927, 1939), but rather to compare certain features of the two instruments and discuss them in relation to modern instrument design.

Consider, first, the method of intensity control that has been used. In each case it was necessary, in order to produce a colour match, to vary the intensities of three beams taken from different parts of the spectrum. Intensity control is a perennial source of trouble to designers of photometric, and especially spectrophotometric and colorimetric, apparatus; in a trichromatic colorimeter the problems may be particularly awkward because whatever device is chosen has to be used in triplicate, and space may prove a serious restriction on the

choice that can be made. Consider the possibilities: (1) the inverse-square law, (2) polarization devices, (3) rotating sectors, (4) variable apertures, (5) photometer wedges, (6) grids.

(1) is excellent when the illumination of a screen is to be varied by varying the distance of a lamp from the screen, but it is usually quite impossible to employ it in the type of apparatus we are considering. (3) is certainly possible in some instruments, and may consist of a series of fixed-aperture sectors or a variable sector, e.g. the type of sector used by Abney in some of his experiments. Fixed-aperture sectors provide probably the most reliable method we have of cutting down the intensity of a beam in some given ratio, and as one stage in the control of the intensity in a spectrophotometer, e.g. in Guild's spectrophotometer (Guild, 1924), it is excellent. But its use in triplicate in a colorimeter is out of the question. Use of (6) may be a possibility in some instruments, when the grids are placed in beams of wide and uniform cross-section, but these are not the conditions that usually obtain in spectrometric apparatus, and in any case the accurate production of fine grids is no easy matter and, so far as I am aware, they are not used extensively.

There are thus three methods remaining, namely, polarization devices, variable apertures, and photometer wedges, and all three have, in fact, been employed in trichromatic colorimeters. Abney controlled his intensities by varying the width of slits placed in the plane of the spectrum; this is, in effect, a variable-aperture method of intensity control. So, too, is the device used in the Donaldson colorimeter (Donaldson, 1935), although, because the areas involved are so much larger, the control is more accurate than that used by Abney. In the Guild colorimeter (Guild, 1925), the variable-area method is also used, but the method is related to the rotating-sector device through the action of the rotating prism. In the Helmholtz colorimeter, which was employed so extensively by König (1903), polarizing prisms are incorporated to vary the intensity, while in my own instrument I have used photometer wedges.

Personally, I have a prejudice against polarization methods in spectrophotometric and colorimetric apparatus, a prejudice which is not, however, shared by everyone; they are undoubtedly easy to operate and possess little irregularity in the intensity-rotation relation, but they are wasteful of light, they are subject to unsuspected sources of error from partial polarization that may have taken place in other parts of the optical system and, without complicating the system by the addition of further polarizing prisms, the intensity scale is very condensed at the low-intensity end. Photometer wedges are very convenient from almost every point of view except that they may not be strictly neutral and, although the intensity variation is closely linear when plotted as density against length of wedge, very exact linearity is only possible with great care in their manufacture. Variation of aperture is also very convenient but, as evidenced by the care required in the Donaldson colorimeter to make special correcting templates, the method cannot automatically be assumed to give accurate intensity control without thorough testing. Certainly, in Abney's case, the area was so small that the accuracy must have been strictly limited, and yet it must have proved a very handy method of control. There does still seem to be an opportunity for someone of an inventive turn of mind to design a simply operated intensity

control, with an open-scale, very smooth calibration curve so that it can be read to a very high accuracy and with neutral transmission with respect to wavelength.

One of the big disadvantages of Abney's apparatus was the rather low intensity of his matching field. This was inevitable because his method of mixing his three primaries was to focus the three pencils on to a diffusing screen. The reduction in brightness compared to that seen when the eye is placed immediately behind the slit in the spectrum is very considerable, and yet the use of a diffusing surface has much to commend it. I certainly envy the ease with which Abney could demonstrate the way in which his three primary beams were being mixed; he had only to hold a card behind his three spectrum slits and gradually withdraw it, when the three beams would be seen first individually and then gradually overlapping. There would be no doubt at all what was going on. Nowadays, nearly all observations are made by looking through a tube—we hardly think it scientific unless we do so—and unless we happen to be familiar with the apparatus, there is usually a good deal of mystery about what is going on inside. I am not advocating that we should forthwith scrap the Maxwellian field of view—that is generally both undesirable and impossible—but there may be occasions when we might dispense with it with advantage, more especially, I believe, in apparatus which we are using for instructional purposes, and particularly instruction in general principles.

When the matching field is projected on a screen, the actual act of observation is very much easier, and this is all to the good in so far as it adds to the comfort of the observer. There is also the advantage that both eyes can be used, as they are, of course, used in everyday observations. But for some observations there is the disadvantage that the diameter of the eye-pupil is uncertain, and hence the amount of light falling on the retina is indefinite. Viewing the field through the exit-pupil of an instrument to some extent overcomes this trouble, but it does not do so completely unless some method is adopted whereby the eye-pupil and instrument-pupil are centred relative to one another and maintained in that position. For, some years ago, Stiles and Crawford (1933) showed that a narrow pencil of light passing centrally through the pupil of the eye causes a greater luminous effect than the same pencil passing near the edge of the pupil. If the exit-pupil of the instrument we are using is fairly small, the apparent brightness of the field will vary as the observer's head moves. This can be prevented most effectively by fixing the head with the dental-impression method used by Stiles and Crawford, and I have, in my colorimeter, provided a mounting to which each observer can clamp his own dental impression and thereby centre and fix his head. Although I first incorporated this for some binocular matching experiments, we now use it for all observations with the colorimeter as a matter of routine, and it is my belief that the consistency of our results has been improved through its use. Certainly, it prevents the appearance of coloured fringes round the field of view, fringes that are sometimes rather disconcerting to the observer, especially the inexperienced colour matcher, and I would urge instrument manufacturers to consider whether it might not prove advisable to use some such fixation device in certain types of visual instrument, particularly those in which the exit-pupil is small or unsymmetrical, e.g. a slit.

Another feature of instrument design that I would like to take up with manufacturers is the general question of size. Because of the need to keep the costs of instruments down to a minimum, manufacturers tend to make their instruments as small as is consistent with satisfactory operation, and if they have made a correct estimate of the economic position, I cannot, of course, quarrel with their decision. But I suspect that in not a few cases they make the instruments small because they like them that way. They are proud of the intricacies of a complicated mechanism and of the compactness of a design. For the research worker, I do not believe this is a correct view to take, and I would like to make a plea for larger instruments, where cost and space permit. As a small example of two equivalent optical systems, consider the optical arrangement at the eyepiece end of my colorimeter. The method I have used is shown in figure 1 (*a*); an alternative

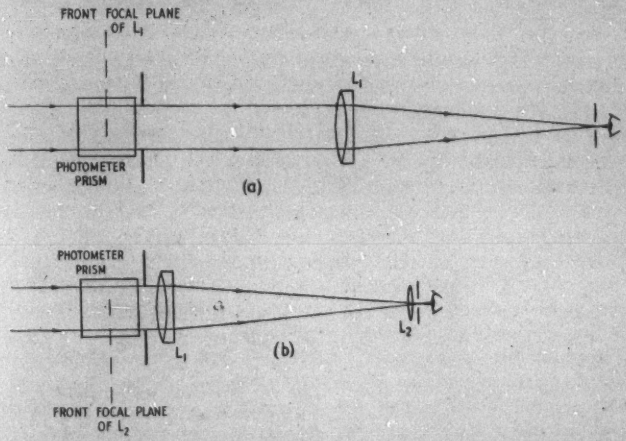

Figure 1.

arrangement is shown in figure 1 (*b*). Each would bring the light to a focus in the plane of the exit-pupil and give the same-sized patch of light in that plane, the photometer prism would be seen in sharp focus and under the same visual angle for an eye focused at infinity, yet the second arrangement is shorter than the first by nearly the focal length of the lens L_1, about 10 inches in my instrument. Yet I have found that extra length very useful, as it has provided me with space for other devices that would have been very difficult to fit in otherwise. In research work, it is impossible to know in the initial stages all the types of observation that may ultimately be made with any given piece of apparatus, and if the manufacturer leaves no space for additions and modifications, then the instrument is to that extent less satisfactory as a research tool.

However that may be, both Abney's instrument and my own have been on a large scale. My original model was a somewhat clumsy apparatus of glass and brass and wood, spreadeagled over a considerable area of benches and tables. In a later model I have built the base from a central cast-iron pillar and heavy

cast-iron arms radiating from the pillar. Although the weight of the optical parts to be supported is quite small, it is important that the various optical parts, situated, as they are, several feet apart, should not move relative to one another. The arrangement I adopted has proved very satisfactory both from the point of view of rigidity and accessibility, and was a great improvement over the earlier model spread over a large flat area. In an instrument costing an amount of the order of £500, I consider £50 a reasonable fraction to spend on a heavy base of this type; that has been my experience, and I mention it because it may be of some interest to others in various research laboratories. The question of cost will, however, take on a different appearance where a complete instrument has to be ordered from a firm, instead of getting the various components made in your own workshop or by small firms outside, and assembling the parts in the laboratory.

I have suffered a good deal of ridicule from my more mechanically-minded friends over my extensive use of strings, weights and pulleys as a means of moving my photometer wedges for colour matching and moving the test-colour prism for hue-discrimination measurements. It would no doubt be possible to design a rack and pinion for each wedge, operated through a flexible cable or by rods linked with universal joints, but I do not believe such a method would give so smooth or easy a movement as that given by a drum with a string wound round in one direction leading to the wedge and in the other direction to a counter-balance weight. Further, in the case of the test-colour prism, this may sometimes have to be moved only a millimetre by one observer in making a just noticeable step, while a colour-blind observer may need 2 or 3 centimetres for a step; or again, the person operating the apparatus may wish to transfer the prism from one end of the spectrum to the other in the space of a few seconds. I do not think these requirements could be met by any rack-and-pinion device without a great complication of mechanical design. I have been told that instrument firms would hesitate before putting an instrument on the market that was operated by strings and pulleys; I would venture to doubt their judgment on this point, if it is a true statement of their views. I would certainly claim that no colorimeter on the market has the three knobs that control the amounts of the primaries in such a convenient position as I have been able to arrange by the aid of my string system.

There is one last point I would like to make on the question of instrument design. I would like to emphasize the advantages that can sometimes be obtained by making use of the high precision that is possible in the manufacture of prisms and lenses. When I built my first instrument, I had not had sufficient experience to realize what might be gained in this way, and as a result, I provided a number of adjustments of the rotating and tilting kind that could have been avoided by improved optical design. In the later model, I incorporated a number of alterations which would take too long to describe in detail, but which included tall dispersing prisms instead of two shorter ones mounted above one another, a front-surface aluminized mirror with a rectangular hole in it to provide two strips of mirror in one plane, instead of two independently mounted reflecting prisms, a photometer prism with its angles made to a high degree of accuracy, so that two beams which are parallel before they enter the prism are parallel

when they leave it, and so on. By means such as these, the new colorimeter was almost automatically in adjustment once the components were assembled in position, and an adjustment that had previously been very awkward, namely, the bringing of the images of the two spectra to a position of coincidence in the plane of the exit-pupil, now followed inevitably from ordinary optical principles, within the limits set by the flatness of the prism surfaces and the mirror surface, and by the aberrations of the corrected lenses employed. Optical instrument makers as a whole naturally appreciate the value of optical tricks of this kind, but I believe there is a tendency among those concerned with the assembly of optical apparatus for experimental and research purposes to provide elaborate and unnecessary mechanical adjustments that make the handling of such apparatus far more difficult and irritating than it need be.

§ 3. THE COLOUR-MIXTURE CURVES

Both Abney and myself were concerned with the measurement of the amounts of the red, green and blue instrument primaries that were needed to match the various colours through the spectrum. Data of this kind are fundamental to any method of colour specification, and the data we recorded at the Imperial College were combined with those obtained by Guild at the National Physical Laboratory to form the basis of the colour-matching characteristics of the normal observer subsequently adopted by international agreement. That is now past history, and there is no need to go over the ground again here. One aspect of these measurements is, however, still of current interest and practical importance, namely, the variation of the colour-matching properties among a group of observers, their differences from the standard observer, and the possibility of correcting small departures from normality so that all measurements would be standard measurements. I would therefore like to discuss our experiments from that point of view, and must first refer to the system of units that I adopted in recording the colour-mixture curves.

When specifying a colour on the trichromatic system, it is not only necessary to define the primaries themselves, e.g. by their wavelength if they are monochromatic colours, but also to define their relative magnitude. It is common practice to do this by making a match on some specified white and adjusting the units so that equal quantities of the primaries are required in the white match. This is perfectly sound practice for colorimetry, when the main aim is to obtain a result as near as possible to that which would be obtained by a normal observer and for which a measuring technique is required that tends to remove the effects of individual differences of colour vision. My interest, on the other hand, was in part to investigate those differences as well as to obtain a mean set of curves, and the use of white to define the primary units has one disadvantage for this purpose. Over a retinal area of some 3° in the foveal and macular regions, there exists a yellow macular pigment that varies in density from one observer to another, and before any light can reach the fovea, it has to pass through this pigment. By the time, therefore, that a pencil of white light of some standard energy distribution reaches the light-sensitive part of the retina, it has become more or less yellow and can no longer be regarded as a standard white. On the other hand, a monochromatic radiation from only a narrow band of the

spectrum could not change in energy distribution as it passed through the yellow pigment, but would merely suffer a reduction in intensity. Yet if the primary units were based on a white match, the white would always be recorded as having the same colour coefficients whatever the density of the pigment, whilst the corrected coefficients of the spectral colours would vary with its density. Such variations would be erroneously put down to differences in the light-sensitive mechanism itself, a misleading conclusion if we hoped to use the data to correct for individual differences in colour vision. The alternative that I used was to base the units on matches on two monochromatic radiations, a yellow at 0·5825 μ for which the red and green units were made equal, and a blue-green at 0·4940 μ for which the green and blue units were equalized. These unit colours were unchanged in colour after their passage through the yellow pigment, hence any differences in the coefficients for the spectral colours that were recorded for different observers could not be due to pigment differences, but were, presumably, due to variations in the response mechanism itself. On the other hand, the effect of pigment variations was all thrown on to the coefficients of the white point, and the position of the white point in the colour chart was, in part at least, an indication of the colour of the macular pigment.

The results of the white-point measurements (Wright, 1928) suggested very strongly that much of the observer variation is due to pigment differences, i.e. considerable variations in its density and slight differences in dominant hue. I have never made any attempt to correct for these differences by means of a yellow or blue filter, but this should certainly be possible, just as correcting filters have been suggested for luminosity measurements (Ives and Kingsbury, 1915). The density of the correcting filter would, of course, have to be determined for each individual by a separate white match. It is generally considered that the density of the pigment increases with the age of the observer, and this is confirmed by my own experience, as my white point has moved during the past 15 years from a position well on the blue side of the average to a point slightly on the yellow side. But it is also true that the pigmentation varies considerably from one individual to another of the same age, so that while each individual may get yellower with age, the starting points will be different for different people. For example, the yellowest point that I obtained from a group of 35 observers was for an observer who was only 20 years of age.

It is difficult to feel so happy about the possibility of correcting for the variations in the colour-response mechanism that are revealed by the differences in the spectral-coefficient curves. It has already been implied that the employment of a colour filter would have no effect on the coefficients of spectral colours, and would not, therefore, achieve the correction required. The most promising line of attack would probably be to find the magnitude of the errors in various parts of the colour diagram and apply suitable corrections; even this would not be completely satisfactory, as the amount of the correction would not be unique for any given point in the colour diagram, since any one colour can be produced by many different energy distributions. Complete elimination of the observer trouble is therefore hardly to be hoped for, and the adoption of substitution methods to reduce the errors to second-order magnitudes should be followed in visual colorimetry.

It is interesting to compare the spectral-coefficient curves obtained by Abney with those just described, when both sets of data are referred to the same primaries and the same units. It then appears (Wright, 1928) that there is surprisingly little difference between the two, so that the doubts about the numerical accuracy of Abney's results are not confirmed. This is very gratifying; the major difference is in the position of his white point, and this might well be expected, since he made no pretence of using a white with a precisely determined colour temperature.

§ 4. COLOUR DISCRIMINATION

One type of observation to which we have devoted a good deal of time is the measurement of the just-noticeable colour difference with change of wavelength or saturation or position across the colour chart. Professor Martin, with the assistance of Mr. Warburton, was the first to carry out such investigations at the Imperial College, in this case on saturation discrimination (1933); since then, data have been recorded on hue discrimination for both normal and colour-blind observers and, quite recently, for the whole area of the C.I.E. colour chart. One of the weaknesses of Abney's work was that he made no observations on the sensitivity of the eye to colour differences; his colour-patch apparatus, unfortunately, did not lend itself to that kind of observation. As a result his conclusions about colour deficiencies were rather incomplete, since weakness in colour discrimination is the most outstanding, and in practice the most serious, feature of colour blindness.

I have only time to deal with the last of our investigations on discrimination (Wright, 1941), which had, as its immediate object, the testing of the standard C.I.E. colour chart (Smith and Guild, 1931) to find the extent to which equal colour differences are represented by equal lengths in the chart. Previous work elsewhere had indicated that the departure from equality would be considerable; but I believe this was the first experimental check of practically the whole area of the chart. We found that equivalent steps in the blue and purple regions of the chart could be represented by quite short lines, but in the green corner the lines were some 20 times longer. This makes the C.I.E. chart an inconvenient diagram for the representation of colour tolerances and for judging the significance of colour differences; the ideal diagram would be one in which a colour tolerance could be specified merely by the radius, r, of a circle drawn about a point C in the diagram, C representing the specified colour and the circle representing the area within which any attempted match of C must lie if it is to be acceptable. There has been much activity in the United States in the last few years aiming at the discovery of an oblique projection of the C.I.E. chart that would give a more uniform distribution of the colours, and when our results were expressed on the Uniform Chromaticity Scale of Breckenridge and Schaub (1939), it was apparent that the steps were very much more nearly equal in size than before, although they still varied in some parts of the chart by as much as 4 : 1. Other data are being recorded in the U.S.A., and when they are all collated, it will be interesting to see whether an improved projection can be found in which the steps are more nearly equal over the complete area. Exact equality is certainly not to be expected. If the suggestion for a change from the present C.I.E.

system as a basis for standard colour specifications is made, the existence of the Colour Group should ensure that the pros and cons will be fully discussed in this country, and in the meantime, it may be advantageous to provide further opportunities for the discussion of the trichromatic colour diagram as a medium for the specification of colour tolerances and the extent to which it is being used for this purpose in practice.

MacAdam (1939) has maintained that tolerances are so often governed by manufacturing considerations, and in any case vary according to the type and conditions of observation, that no single chart could serve as a uniform scale for all cases. For this reason he considers that the C.I.E. chart should be retained. In a recent paper (Wright, 1941) I ventured to doubt whether the conditions of observation would cause any significant change in the relative size of the steps, and whether this could be used as an argument against a change of system. Since then, however, I have had occasion to make some hue-discrimination observations when the two comparison fields consisted of very small circular apertures separated by an angle of 1°. The angular size of the geometrical images of the two apertures was only 6′, but this was enlarged somewhat by diffraction, especially as they were viewed through an exit-pupil of 1 mm. The results showed that, in comparison with those obtained with a 2° field, the size of step as measured by wavelength difference increased in the blue-green to a greater extent than in the orange, the relative change being by a factor of the order of 2:1. As a matter of interest, this supports current practice in the choice of red as the ideal signal colour and the absence of both blue and green together in any one signalling system. The change in observing conditions is, however, rather extreme and might not be considered to affect the main issue about the merits of a change in the C.I.E. system, since small point sources are not typical test objects and are of no concern, for instance, to the dyeing or paint industry. Yet the effect is of some interest, for at the present time the specification of the colour of signal glasses and their tolerances is the most outstanding example of colour limits being expressed on the trichromatic system and the one most frequently used for illustration purposes in papers on the subject. To this extent, therefore, MacAdam can find support for his contentions, and there may, of course, be other examples of the same nature. Obviously the subject will be a fruitful source of discussion in the future.

§5. SUBJECTS FOR FUTURE RESEARCH

That gives me the cue for the final remarks I wish to make. What are the most fruitful lines of research on colour to follow during, say, the next 10 years and, since this is an account of work at the Imperial College, what problems should we seek to solve here? I am not now thinking of problems in colour vision; I have made no reference to the researches we have carried out that have had primarily a physiological bias, and there is little difficulty in planning a programme of work on visual subjects that would last for several decades. But in the physics of colour there may be some suggestion that most of the work has been accomplished with the adoption and general acceptance of the characteristics of the standard observer, although this is not my own view. There are certain matters to be tidied up, such as the tolerance question to which I have already

referred, and other matters, such as the colour-matching characteristics of the extra-fovea, which should be of some colorimetric interest in connection with the use of large matching fields. These, however, are comparatively minor problems compared to the subject which seems certain to occupy our attention for many years to come, namely, spectrophotometry, and, in particular, photoelectric spectrophotometry. The United States are a long way ahead of us in this field, and the extensive use they are making of the method is an indication of its importance in industry. It is not as a means of colour measurement that its chief advantage lies, but rather as a method of following the effects of subtractive colour mixture. This includes most of the industrial applications of colour—dyeing, painting, printing, colour photography and so on; innumerable technical problems must arise in these industries, and in addition, there are highly academic problems of molecular structure, the relation between the chemical constitution of a substance and its absorption curve, the manner in which colouring materials are associated with the substances they colour, all subjects that call for close collaboration between physicist and chemist. I am hoping that we shall be able to help with the physics of these problems. There are ample problems to go round among the various organizations that have a legitimate interest in them, although I anticipate there will be a good deal of competition to acquire the first recording spectrophotometer that becomes available in this country, a competition for which I hope the Imperial College will at least be able to enter.

In preparing this lecture, I have been fortunate in being able to draw on material that has accumulated for over 65 years and inevitably I have had to restrict my remarks to a few isolated aspects of the work. I imagine, however, that nearly everyone in the Colour Group could prepare an interesting account of his own experiences from which we could all learn something, and it is my sincere hope that, as occasion arises, members of the Group will come forward and assist us in that way.

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X-RAY STUDY OF CRYSTAL DYNAMICS: AN HISTORICAL AND CRITICAL SURVEY OF EXPERIMENT AND THEORY

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ABSTRACT. An outline is given of the reciprocal-lattice method of relating x-ray reflections to the density distribution in the crystal. The experimental work of Laval, Preston, Zachariasen, Raman and Nilakantan, Lonsdale and Smith, and others, is described in some detail, and it is shown that a spreading of the reflecting power outside the reciprocal-lattice points is proved. The main features of this extension of reflecting power are (1) that it is markedly dependent upon temperature, (2) that the surfaces of equal reflecting power are not spherical, (3) that the intensity of extra reflection is weak even in the neighbourhood of the reciprocal-lattice points, and falls off rapidly with distance from the lattice points. The simple diffraction theory, the Faxén-Waller theory and the Raman theory are briefly sketched and related to recent experimental work, and the necessity for distinguishing effects due to dynamic and static disorder of the crystal structure is emphasized. A description is given of the anomalous effects found for diamond, and finally it is shown that only the Faxén-Waller theory, which explains the spread of reflecting power as due, in the main, to the thermal (elastic) vibrations of the atoms and molecules, can account satisfactorily for the results observed for crystals of all kinds, and especially for single crystals of metals. The limitations of the theory, especially in respect to its assumption of small amplitudes of vibration, are indicated, and possible future developments are outlined.

§1. INTRODUCTION

The sharply defined spots on any x-ray crystal photograph will, if properly interpreted, give a partial or complete picture of the crystal as a three-dimensional diffraction grating composed of a regular arrangement of stationary atoms. It is well known, however, that the atoms are not stationary but oscillating, and that the picture, therefore, gives only the mean atomic positions. The dynamics of crystal lattices have been studied theoretically by Born and others (1912, 1913, 1933), and the x-ray interference effects due to the heat motions of the atoms were the subject of an early theoretical investigation by Debye (1914), who predicted a reduction of intensity of all normal reflections and a general background scattering independent of crystal orientation. These conclusions were supposedly confirmed by subsequent experimental observations (Jauncey, 1922 ; Jauncey and May, 1924 ; Woo, 1931; Coven, 1932; etc.) which we now know were made under unsuitable conditions.

When the intensities of x-ray reflection from the planes of the crystal lattice are measured and the structure factors calculated for purposes of structure analysis, allowance is always made for a reduction in intensity due to the heat movements, and it has long been realized that even after such corrections have

been made, the electron-density map given by the most refined Fourier analysis of the crystal structure is blurred by these heat movements, since not only has each measured term of the Fourier series been reduced by a factor which can be expressed as an exponential function of temperature, but some of the later terms of the series have been thereby reduced below the measurable limit. For a really sharp and accurate Fourier contour map of the crystal, measurements of intensity would have to be made at very low temperatures, using X rays of various wave-lengths down to the shortest obtainable (Brill, Grimm, Hermann and Peters, 1939).

Very well-exposed photographs sometimes, however, show spots and streaks which are not part of the normal diffraction pattern at all. These have received various names to distinguish them from the Bragg spots (due to normal reflection by X rays of wave-length characteristic of the target used) and the Laue spots (due to normal reflection by " white " X radiation not characteristic of the target used). They have been called *diffuse*, *anomalous*, *extra*, *subsidiary*, *background*, *temperature*, *modified*, *dynamic*, *quantum*, *non-Laue* and *associated* reflections. (Research workers have occasionally referred to these reflections as *Preston* or *Raman* reflections. For reasons which will be made clear later in this survey, neither of these names has been generally adopted.) Since not all the observed effects are of similar origin, the most suitable term to use here will be *extra reflections*.

§ 2. THE RECIPROCAL LATTICE

In order to relate the observed X-ray diffraction effects to the static structure of the crystal, the use of the mathematical concept of " reciprocal space " (Ewald, 1921; Bernal, 1926) is helpful. In reciprocal space each set of infinite

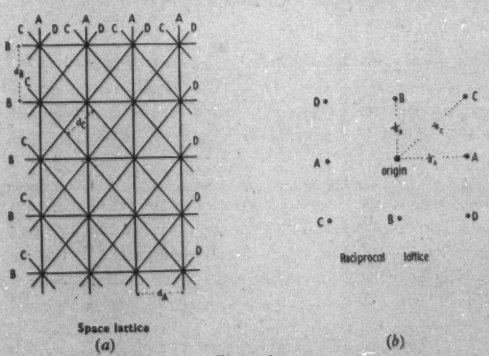


Figure 1.

regular planes, of spacing d, in the real crystal is represented by a point (see figure 1), whose distance from the origin is $1/d$ and whose radius vector lies along the direction of the normal to the planes. The nth order planes, of spacing d/n, will be represented by points along the same radius vector, but at n times the distance (that is, at n/d) from the origin. A development of this representa-

tion leads to the result that, corresponding to all the orders of all the sets of infinite, regular planes in the real crystal, there will be a regular, infinite lattice of points in reciprocal space.

The usefulness of the reciprocal-lattice idea is most apparent when an x-ray photograph has to be interpreted. The fact is, that any x-ray photograph resembles the reciprocal lattice of the crystal much more closely than it does the real crystal. For instance, each spot (point) on the photograph corresponds to a set of planes in the real crystal, but to a point in the reciprocal lattice. The nearer the spot is to the origin (that is, to the trace of the undeviated incident beam) the larger is the spacing of the corresponding set of planes, while the higher the order of reflection, the farther is the corresponding spot on the photograph from the origin. These reciprocal relationships are the result of the Bragg law of reflection $\lambda = 2 . d/n . \sin \theta$, according to which $\sin \theta \propto n/d$ for radiation of a given wave-length λ. The Bragg law is given a very simple geometrical interpretation in terms of reciprocal space (figures 2 and 3). Through the

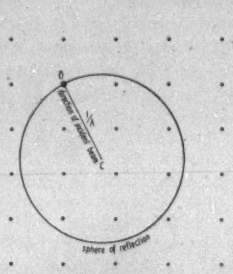


Figure 2.

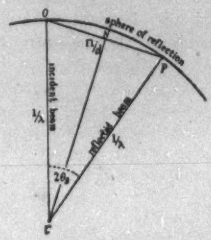


Figure 3.

origin O of reciprocal space let a sphere be drawn, whose radius is $1/\lambda$ and whose centre C is at a distance $1/\lambda$ from O in an arbitrary direction. Suppose that some other reciprocal lattice point P lies also on the sphere. If $OP = n/d$, and the angle OCP be called 2θ, then it is obvious that

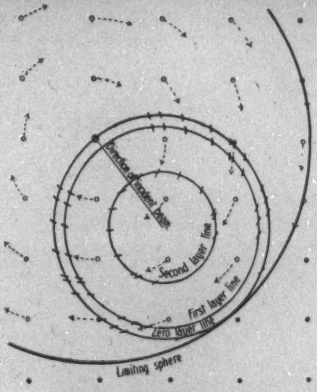
$$\sin OCN = \sin PCN = \sin \theta = n\lambda/2d,$$

and CN, the normal to OP, must be parallel to the set of planes reciprocal to P. Thus any point P which lies on the sphere may be said to obey Bragg's law, the direction CO being that of the incident beam and CP that of the reflected beam. The sphere itself is known as the sphere of reflection, and each point in the reciprocal lattice has an intrinsic reflecting power depending upon the structure of the crystal.

If λ and d are comparable, then for any arbitrary direction of the incident beam CO, the sphere of reflection will not *in general* pass through any points of the reciprocal lattice other than the origin (figure 2). In other words, a monochromatic x-ray photograph of a crystal which is arbitrarily set in any stationary position will in general be quite blank except for the trace of the undeviated incident beam. Various devices are in practice adopted in order to obtain reflections from a crystal; some of these are now described.

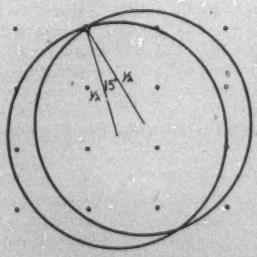
Methods for use with characteristic or monochromatized radiation; (rotation, oscillation or powder methods)

(1) The crystal may be *rotated* about an axis normal to the incident beam. Each point in the reciprocal lattice traces out a circular path about this axis, and in doing so intersects the sphere of reflection twice in each complete rotation (providing, of course,



∘ points which reflect during rotation.
• points outside limiting sphere, which cannot reflect.

Figure 4. Rotation method.



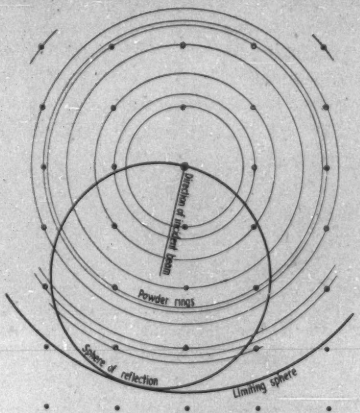
∘ points reflecting during oscillation of 15°.
• points not reflecting during oscillation.

Figure 5. Oscillation method.

that it lies within the limiting sphere, for which $\sin\theta=1$). If the direction of the incident beam lies in one of the main nets, or layers, of the reciprocal lattice, then all the reflecting points in that net intersect the sphere on the equator. Successive nets of the reciprocal lattice intersect the sphere in successive parallel small circles. These, projected on to

a cylinder or a plane placed parallel to the axis of rotation, give the layer-lines typical of such rotation photographs. In the case of a plane photograph it is not, of course, necessary for the plate or film to be perpendicular to the incident beam.

(2) The crystal may be *oscillated* through a known angle about an axis normal to the incident beam. The oscillation of the reciprocal lattice is equivalent to an oscillation of the sphere of reflection. Only the limited number of points in the reciprocal lattice which lie between the limiting positions of the sphere of reflection will reflect, and the reflection of each point will occupy only a limited fraction of the time of the oscillation. An oscillation photograph is equivalent to part of a complete rotation photograph (plates 2 (*b*), 3 (*b*).)



• points which contribute to powder rings.
• points outside limiting sphere, which cannot reflect.

Figure 6. Powder method.

(3) A crystal *powder* may be used, the separate crystallites being uniformly oriented in all directions. Each reciprocal-lattice point becomes a sphere of radius n/d whose centre is the origin, and all such spheres intersect the sphere of reflection in a set of concentric circles. The typical powder photograph is obtained by projecting these circles on to a cylindrical film (usually a narrow strip) or on to a plane film which is normal to the incident beam. If the film is not normal to the incident beam, the powder curves become ellipses or even open conics (Lonsdale and Smith, 1941 a).

Method for use with white radiation (*Laue method*)

(4) The crystal itself may be kept stationary provided that a continuous range of x-ray wave-lengths is used. This range may, but need not, include those wave-lengths characteristic of the target. The minimum wave-length from an x-ray tube depends on the applied voltage, but is usually of the order of 0·35 A. (corresponding to a large sphere of reflection), while the maximum will be, perhaps, more than ten times as long (too long for reflection from any crystal plane). The intensity of the continuous radiation is by no means uniform. Quite apart from the possible excitation of characteristic radiation, the continuous-radiation curve shows a very broad hump of maximum intensity in the short wave-length region. All reciprocal-lattice points lying between the spheres of reflection of maximum and minimum radius will reflect during the whole time of exposure, but the intensities of the reflections will depend upon the wave-length utilized as well as upon the intrinsic reflecting power of the lattice point. Any reflections due to characteristic radiation will be of outstanding intensity.

If the incident beam lies along a symmetry axis or in a symmetry plane of the crystal, a Laue photograph taken on a plate or film placed perpendicular to the beam will reveal the appropriate crystal symmetry, and some beautiful patterns may be obtained in this way.

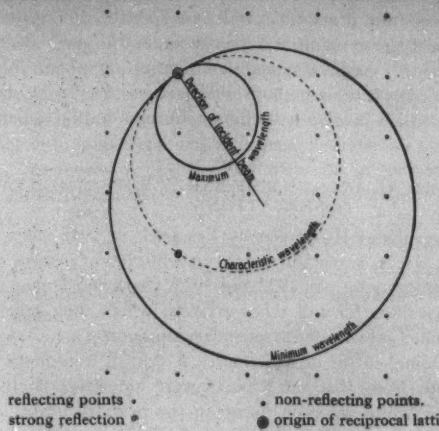


Figure 7. Laue method.

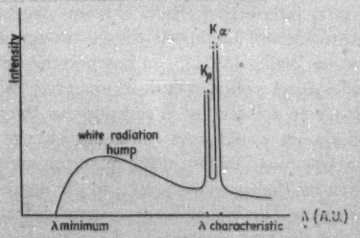


Figure 8.

It is not, of course, necessary to employ a photographic method of recording the reflections. Such methods have the advantage of giving a rapid survey and a permanent record, in a small space, of a large number of reflections, but the ionization spectrometer method may be a more accurate way of measuring exact intensity relationships.

Application of reciprocal-lattice methods to finite and irregular crystals

Since it is clear that in practice a crystal is neither infinite in extent nor perfectly regular in structure (the atomic oscillations alone must partially destroy such regularity), the question may be raised as to whether it is still justifiable to use the reciprocal-lattice method to represent finite or irregular sets of planes. This question receives an affirmative answer from the work of Laue (1936), Ewald (1940) and other mathematical physicists. The reciprocal method may be applied to any density distribution whatever, but unless there are infinite, regular sets of planes in existence, there cannot be a unique lattice of reflecting

points in reciprocal space. The *limiting* of the planes in any direction in real space will lead to an *extension* of reflecting power of each point, along that direction in reciprocal space. Similarly, a disturbance of the regularity of the planes in real space, whatever form it may take, will cause a reduction of the reflecting power at the reciprocal-lattice points and the appearance of new reflecting points in their neighbourhood. Such a spreading of reflecting power in reciprocal space has been observed by various methods and has received a variety of theoretical explanations, all of which involve a limitation of size or of regularity of the crystal lattice.

§3. HISTORICAL ACCOUNT OF EARLY EXPERIMENTAL OBSERVATIONS

On Laue photographs of KCl taken by Friedrich in 1913, there appeared radial streaks which were not part of the normal diffraction pattern and which were not explained at the time. In 1922 and 1923, Clark and Duane discovered anomalous reflections from KI and other crystals, which they called x peaks, and which they explained as being due to secondary emission of *x rays characteristic of atoms* (such as iodine) *in the crystal itself*. A critical examination of their experimental method shows that the x peaks were almost certainly *extra reflections* given by the white radiation hump in the primary beam. Attempts to observe the x peaks photographically (Wyckoff, 1923) showed only smeared-out and indefinite maxima. In 1923 Faxén suggested that the Friedrich streaks might be due to the x-ray interference effects of atoms displaced by heat motion from their normal positions, and his theory, which was applied to cubic crystals only, was generalized by Waller (1925), and has become known as the Faxén-Waller theory. Waller used semi-classical arguments ; his theory was confirmed by Laue (1926), who pointed out in addition that the secondary radiation scattered by a moving atom would have suffered a change of frequency. In 1935 the theory was re-examined by Ott, using quantum methods, and he found that the formulae given by Waller were correct, to the degree of approximation adopted in the treatment. The Faxén-Waller theory differed from the Debye theory in predicting that the heat movements of the atoms would give intensity maxima, weak and diffuse by comparison with the Bragg reflections, but definitely dependent upon crystal orientation. In 1938 Laval, who saw the experimental implications of the Faxén-Waller theory perhaps more clearly than did the mathematicians themselves, planned and successfully carried out an ambitious scheme of research to determine whether the Debye or the Faxén-Waller theory most nearly corresponded to the experimental facts. He realized that the extra intensity maxima, if present at all, would persist even when the crystal was not in the proper reflecting position for a Bragg reflection, and he therefore looked for them using an ionization spectrometer method, monochromatizing his radiation (CuKα and MoKα) and arranging to be able to turn his crystal specimens into any desired orientation. Laval, whose work was carried out in Prof. Mauguin's laboratory, published a preliminary account of the results in the *Comptes rendus* in 1938, and a full account in the *Bull. Soc. Franç. Min.* in early 1939. Unfortunately the latter journal is not an easily accessible one to most physicists; his work was therefore overlooked for some time, and has not yet

received the attention it deserves (see, however, Jauncey and Baltzer, 1941; W. L. Bragg, 1941; Lonsdale and Smith, 1941). It is all the more important to emphasize that Laval discovered nearly all the major experimental facts concerning the extra reflections, and that he did so as the result of a well planned scheme of research. He found (1) that discrete intensity maxima as predicted by the Faxén-Waller theory do actually exist; (2) that they can be observed by using monochromatic (characteristic) radiation with the crystal in positions not far from the Bragg setting for any given plane; (3) that their intensity (of which he obtained absolute measurements) is in general much less than that of the Bragg reflections, but increases considerably with rise in temperature; (4) that the intensity rapidly diminishes as the crystal is moved away from the Bragg setting (he gave various intensity curves showing this effect), but (5) that in the Bragg setting the extra reflection forms a shoulder on all sides of the Bragg reflection (he used a powdered specimen of silver to illustrate the broadening effect on the powder reflections). (6) He pointed out that this extra reflection corresponded

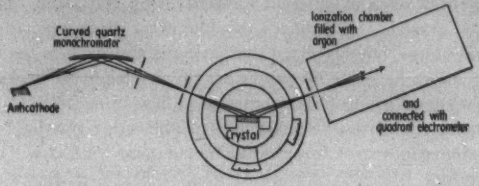


Figure 9. Laval's apparatus (*Bull. Soc. Franç. Min.* **62**, 139 (1939)).

to a spreading of reflecting power in reciprocal space around each reciprocal lattice point, and (7) by measuring the contours of the "isodiffusion surfaces" (surfaces of equi-reflecting power) about some Bragg reflections he showed that these surfaces are not spherical. (8) He showed that in some cases there was an extension of reflecting power right across from one reciprocal-lattice point to another, and (9) that the intensity of extra reflection for high orders was greater than it should be if extra and Bragg reflections obeyed the same law of intensity decay. (He found the following intensity values, referred in each case to a maximum of 100, for the first five observable orders of the KCl cube plane:—

Bragg reflection: 100:20: 7: 3: 1
Extra reflection: 100:50:33:21:12

at a constant angle of deviation from the appropriate Bragg setting for each extra reflection.) (10) He observed that, in general, the extra reflections varied in sharpness and intensity from one substance to another, even for planes of equal intrinsic reflecting power; and finally (11) he measured the weak background intensity which is due to incoherently scattered radiation of the Compton type and also to extra reflection of wave-lengths other than those characteristic of the target. (Such unwanted wave-lengths are present even in a "mono-

chromatized " beam, sometimes to the extent of 1 per cent or more: cf. Robinson (1933).) Laval did not apparently observe the geometrical shifts which are a feature of the extra reflections from some crystals, and he examined only elements and ionic compounds, but there is no doubt that had his results been easily available to physicists at the time of their publication, they would have aroused considerable interest and would have prevented subsequent claims for priority which have unfortunately been made.

Independently, and only a few months later, Preston (1939), while investigating the age-hardening of Cu—Al alloys by x-ray methods, observed on Laue photographs of pure Al, taken with radiation from a silver target, some weak spots which were not part of the normal diffraction pattern from such a face-centred cubic crystal. The intensity of these extra spots was enormously enhanced by raising the temperature of the specimen to 500° c.; and when the radiation was monochromatized, the extra spots remained, although all Laue spots disappeared. He found similar temperature-sensitive extra spots on Laue photographs taken in different settings, using NaCl and MgO as well as the original Al crystal. He believed that the extra spots were due to the heat motions of the atoms, but suggested that a simple approach to the theory of the phenomenon might be made by supposing the crystal to be broken up by the heat waves into small groups, each containing a few atoms all scattering in phase, each group being slightly out of phase with neighbouring groups. This method has been developed into the "simple diffraction method", which will be considered in a later section.

In 1938, Wadland, in America, had also found unexpected streaks and spots on Laue photographs of NaCl and KCl taken with tungsten radiation. He offered no explanation of these extra reflections, but Zachariasen (1938) suggested that they might be due to two-dimensional diffraction effects in the surface layer of the crystals. Late in 1939, however, at a meeting of the American Physical Society, Zachariasen withdrew this suggestion in favour of the Faxén-Waller theory, of which he offered a simplified, but admittedly less precise, derivation. The formulae he obtained included an estimate not only of the position, but of the half-width and intensity variation with increasing deviation from the Bragg setting. These formulae were compared with experiment, but although agreement was obtained in some test cases (Zachariasen, 1940; Siegel and Zachariasen, 1940; Siegel, 1941), the fact remained that since his formulae neglected the difference of velocities of elastic waves travelling in various directions in the crystal, they could, at best, only be expected to give a very rough approximation to the truth. He has since improved them by introducing the velocities and polarizations of the waves (Zachariasen, 1941 b; Jauncey, Baltzer and Miller, 1941).

Early in 1940, Sir C. V. Raman and P. Nilakantan, in an attempt to determine whether there is any x-ray effect analogous to the Raman effect in light-scattering from crystals, discovered extra reflections on Laue photographs of diamond, which they published as evidence of a supposedly new phenomenon. These extra reflections were rather sharper than those found by Preston for Al, NaCl, etc., but were similar in that each was associated with a normal Bragg or Laue reflection and was given by the *characteristic* radiation from the target used.

Raman supposed that the incident x rays excited a characteristic (Einstein, infra-red) vibration of the crystal in all the unit cells simultaneously, but with slightly varying phase from one unit cell to the next, resulting in a coherent reflection of x rays of changed frequency by the "phase-waves" in the crystal. This theory, which will be considered in more detail later, has become known as the Raman theory. Raman and Nilakantan (1940, 1941) also published Laue photographs of sodium nitrate, rocksalt and calcite, and confirmed many of Laval's experimental conclusions, of which, however, they were unfortunately quite unaware. One important result which they established experimentally is that the temperature changes of intensity of the extra reflections and of the Bragg reflections not only vary considerably from one substance to another, but may even vary from one plane to another of the same crystal.

Laue photographs of organic compounds, if well exposed, sometimes show exceedingly strong extra reflections, and these have been studied by Lonsdale and Smith (1941), who have shown that they are similar in every respect to those given by ionic compounds and by metals and other elements. The photographs which illustrate this lecture show various features of the phenomenon, which may be summarized briefly as follows:—

(1) The symmetry of the Laue pattern, if any, is reproduced in the pattern of extra reflections; but the "extra" pattern retains a measure of symmetry even when that of the Laue pattern has been completely removed by a small rotation of the crystal.

(2) The use of monochromatized radiation, which removes the Laue reflections and a good deal of the general background, leaves the extra reflections unaffected and considerably improves the conditions under which they can be seen and studied. It is noticeable that on a monochromatic photograph, however well exposed, little or no diffuse halo appears round the central spot, nor are there, in general, any radial streaks. The difficulty in obtaining good monochromatic photographs is almost entirely a question of exposure (time × intensity) (Gregg and Gingrich, 1941).

(3) The positions of the extra spots on a Laue photograph correspond closely (though not necessarily exactly) to the positions of the Bragg spots on an oscillation photograph taken with the Laue position as centre of oscillation. By a comparison of exposure times (remembering that the extra reflection is being recorded for the whole time of the Laue photograph, but that the Bragg reflection only occupies a fraction of the period of oscillation), it may be seen that the extra reflection is, in fact, very much less intense than the corresponding Bragg reflection, usually of the order of 0·01 to 0·0002 of the latter.

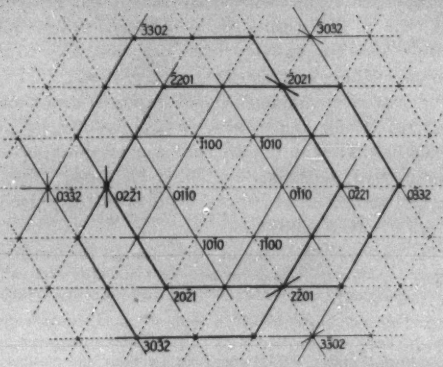
(4) The intensity of the extra reflection is greatest in the Bragg setting for a particular plane (it is then visible on a well exposed photograph only as a halo or background extension of the Bragg spot) and decreases rapidly as the angle of deviation varies in either direction. An extra reflection can sometimes be observed on successive photographs even when the crystal has been turned (say 1° at a time) through as much as 30° altogether. Such large reflecting regions are especially typical of "layer" planes (plates 4 (*a*), 5 (*b*)).

(5) A reduction of temperature to about −180° c. causes a disappearance or considerable weakening in intensity of most of the diffuse extra reflections (plates 5 and 7); this does not apply to the sharp extra reflections which are a feature of normal (type I) diamonds, and which are also sometimes associated with strained-surface phenomena. These will be considered separately later. All temperature changes are reversible.

(6) The resemblance between the monochromatic Cu Kα Laue photograph of benzil, taken with the incident beam along the principal axis (plate 1 (*b*)) and the reciprocal lattice viewed along the same direction (figure 10) is so striking that the propriety of using the reciprocal-lattice method of studying these reflections can hardly be questioned. The comparison shows that the extra reflections in the form of streaks or spots correspond to the intersections of certain *planes* and *axes* of the reciprocal lattice with the sphere of

reflection. There are no streaks corresponding to planes passing through the origin. Most of the observed streaks extend continuously from one spot to the next, thus confirming Laval's observation that the reflecting power can extend in some cases right from one reciprocal-lattice point to the next.

In general, the main experimental facts established by the earlier work point to a weak spreading of reflecting power around each reciprocal-lattice point, sometimes coupled with a differential extension along certain reciprocal-lattice planes and axes. This extra reflecting power is markedly affected by temperature in a reversible way, but that fact alone would not justify our concluding that



_____ reciprocal-lattice planes which correspond to " extra " streaks.
..... reciprocal-lattice planes which do not correspond to " extra " streaks.

Figure 10. Incident beam along alternating hexagonal axis of benzil single crystal (normal to plane of paper). Compare plate 1 (*b*).

the effect is simply due to the temperature movements of the atoms. It might possibly be due to some structural arrangement or to some physical property of the crystals which is changed or affected by those heat movements.

§ 4. SIMPLE DIFFRACTION THEORY

It is a well known fact that if the particles of which a crystal powder is composed are exceedingly small (10^{-6} cm. or less in average diameter) the x-ray powder reflections are broadened. Indeed, this method is used as a means of measuring the size of colloidal particles. Laue and Riewe (1936) have discussed the diffraction effects to be expected from finite crystalline particles, and their results were extended and presented in a new way by Ewald at the Physical Society's 1939 (Bristol) Conference on the Solid State. For a crystal particle of any limited shape, the reflecting power in reciprocal space is not confined to sharp points, but is extended along directions normal to the boundary planes of the particle. Thus the regions in reciprocal space corresponding to a crystal of needle shape are discs normal to the length of the needle, and conversely a disc-shaped crystal will have needle-like reflecting regions instead of points in reciprocal space. As long as the particle is not so small that the parameters of the internal structure are comparable with the dimensions of the external form, a spherical particle will have spherical regions of reflecting power in reciprocal space.

One most important point to notice is that *all the reflecting regions in reciprocal space corresponding to a finite crystal particle* (or to an assemblage of finite, parallel, but independent crystal particles) *will be similar and similarly oriented.*

If a large, apparently single, crystal is actually composed of very small parallel crystallites, the reflecting regions in reciprocal space, besides being similar and similarly oriented, will be entirely diffuse. There will be no sharply defined reflecting regions such as are indicated by the sharp Laue spots. If the crystal is made up of a mixture of large and very small crystallites there will be sharp reflecting regions, each with an extended diffuse background.

The result of supposing, as Preston did, that the crystal diffracts not as a whole but as a system of small blocks all slightly disoriented with respect to the average crystal directions or having slightly different spacings, is to postulate the existence of a number of reciprocal lattices of slightly differing sizes and orientations, all having entirely diffuse reflecting regions. Near to the common origin the

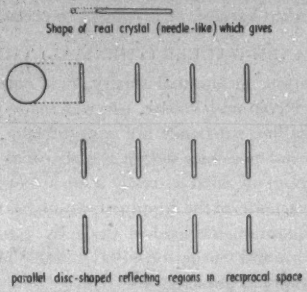


Figure 11.

superposed diffuse reflecting regions will be rather similar to those of a system of parallel small crystallites of uniform spacing, but regions farther from the origin will be extremely diffuse and extended. This is not at all in agreement with experiment.

The method has been developed by Sir W. H. Bragg (1940, 1941), who has shown that a great many of the observed phenomena can be geometrically accounted for by postulating the existence of two-dimensional sheets of atoms in the crystal, all x-ray scattering from the atoms in any one sheet being in phase, but with a random phase-relationship between such sheets and the remainder of the crystal. The reciprocal-lattice method was not used by Sir W. H. Bragg, who calculated the diffraction effects directly, but it may readily be seen that such sheets in real space correspond to intensity spikes in perpendicular directions in reciprocal space and that, by symmetry, any one such spike parallel, say, to the [110] direction of a cubic crystal must be accompanied by spikes along all crystallographically equivalent directions, for each reciprocal-lattice point.

Now it will be shown that the experimental data do, in fact, correspond either to ellipsoidal regions having their main axes along certain main crystallographic directions, or to intensity spikes along certain of these directions in reciprocal space; and up to a point, therefore, it will certainly be possible, by choosing suitable groups or arrangements of atoms scattering in phase with

each other, but out of phase with their neighbours, to explain observed experimental effects. It is found, however, that in explaining those extra spots that *are* observed, the theory also predicts some extra spots of equal or greater intensity, which are definitely not present. Nor is it possible, by means of the theory, to predict the detail of the extra reflections for unknown crystals even of the simplest composition or structural arrangement. As it stands, the simple diffraction theory does not explain why all body-centred cubic metals do not behave similarly, nor why face-centred cubic metals may or may not behave like body-centred cubic metals. Nor does it appear to offer any adequate explanation of the large temperature changes of intensity which occur.

Nevertheless, it will be seen later that this theory, although inadequate to explain all the effects, has a certain significance; and some form of the theory probably provides the correct explanation of those temperature-independent, structure-sensitive extra spots which appear when the crystal investigated has a freshly cleaved or worked surface, or is subject to certain types of strain.

§5. FAXÉN-WALLER (THERMAL) THEORY

In the elastic-vibration, or thermal theory, first correctly developed along semi-classical lines by Faxén and Waller, use was made of the known fact that the atoms of any crystalline substance are continuously in motion about their mean positions. It is not possible, within the scope of a survey of this kind, to give a rigorous account of what is really a most complicated mathematical treatment, but the salient points of the argument, which has been further elaborated and given a strictly quantum-mechanical basis by Laue (1926), Ott (1935), Zachariasen (1941), Born and Sarginson (1941, 1942), Jahn (1942) and others, will here be given as simply as possible.

The principal assumption made is that the forces in the crystal are harmonic. The frequency of the atomic vibrations (say 10^{13} sec.$^{-1}$ or less) is very low compared with that of the x rays (about 10^{18} sec.$^{-1}$). To the incident x rays, therefore, the crystal will appear to be stationary, but with the atoms displaced unequally from their mean positions. These atomic displacements can be resolved into a system of standing waves superimposed upon the regular crystalline structure. The time-integrated effect of any one wave can then be considered separately, and the results of all the waves added together.

The structure factor (and hence the intensity of reflecting power, which is proportional to the square of the structure factor) of any set of parallel planes (*hkl*) depends upon the relative positions of the atoms in the direction normal to the planes. The structure factor will be changed if the atoms change their positions in respect of their relative distances from the planes, but not if they merely move parallel to the planes. It may be shown that in the case of a harmonic vibration in which the atomic movements are *normal* to a given set of planes, the resulting change in the intensity of reflecting power is, to a first approximation, proportional to the *mean-square amplitude*, $\overline{\xi^2}$, of the oscillation. The mean energy of an oscillator, $\overline{E}$, is proportional to $\nu^2\overline{\xi^2}$, where ν is the frequency, and $\overline{E}$ for a Planck oscillator is

$$h\nu\left(\frac{1}{2}+\frac{1}{e^{h\nu/kT}-1}\right).$$

If $h\nu \ll kT$, $\bar{E}$ therefore approximates to kT. *The intensity change of reflecting power* due to the oscillation is therefore proportional to kT/ν^2, and *is greater the lower the frequency*.

The possible vibrations of a lattice may be roughly classed as of two kinds: the acoustical vibrations, in which neighbouring atoms move, in general, in the same direction, and the optical vibrations, in which neighbouring atoms move, in general, in opposite directions. In both cases, the frequency of the vibration is a function of its wave-length, but in the case of the acoustical vibrations the frequency becomes zero for certain values of the wave-length, while for the optical vibrations the frequency is never less than a rather high minimum (which may or may not be less than the maximum acoustical frequency *).

Since it is the lowest frequencies which correspond to the largest amplitudes, and which are, therefore, of greatest importance in assessing the intensity changes due to the atomic vibrations, and since these lower frequencies are entirely

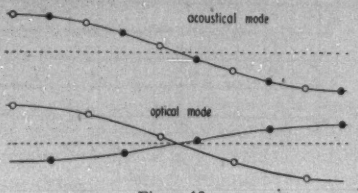


Figure 12.

those of the acoustical spectra, it is only the acoustical (or elastic) vibrations which need be considered in the first instance. A complete theory of the effect must, however, take account of the whole frequency spectrum, including both acoustical and optical branches, which are not always distinguishable from each other.

The frequency of a single wave is equal to its velocity divided by its wave-length. The velocity of an elastic wave of given wave-length, travelling in any given crystal direction, is determined only by the wave-length, the density and elastic constants of the crystal, and the polarization of the wave. The wave-length can, in practice, vary from infinity down to a length comparable with the unit-cell size. Along certain main crystal directions, the elastic waves can be resolved into three components, two transverse and one longitudinal; but, in general, such a resolution is not possible.

Let us, to take a simple case, consider the effect of a transverse stationary vibration whose wave-length μ is along the [100] direction of a cubic crystal (figure 13). Clearly there is no atom along [100] which exactly repeats the conditions at A until we come to A′, which is one wave-length away. The effect of the stationary wave is to impose a super-lattice on the original structure, the dimensions of the super-lattice being dependent upon the wave-length and direction of the stationary wave (in figure 13, μ is assumed, for the sake of convenience, to be an integral multiple of the lattice spacing, but this is not necessary).

* For a more precise account of lattice vibrations see Born and Kármán (1912), Born and Göppert-Mayer (1933) or the paper by Professor Born on p. 362 of this issue.

In the super-lattice, though not in the original lattice, there will be planes AB′, AC′ which are nearly of the same orientation as the plane AA′, and *also nearly of the same spacing*. The longer the wave-length μ, the nearer is this approximation. To a first approximation, only the one pair of planes, AB′ and AC′, in the super-lattice, will give reflections of appreciable intensity, and thus the result of the stationary wave is to introduce a pair of "ghost" reflections, one on each side of the original reflection from AA′. In reciprocal space there will be, on each side of the lattice point P corresponding to the set of planes AA′, a weakly reflecting point whose distance from P is $1/\mu$; in fact, this will be true for every lattice point, but the intensity of the ghosts will vary with the points.

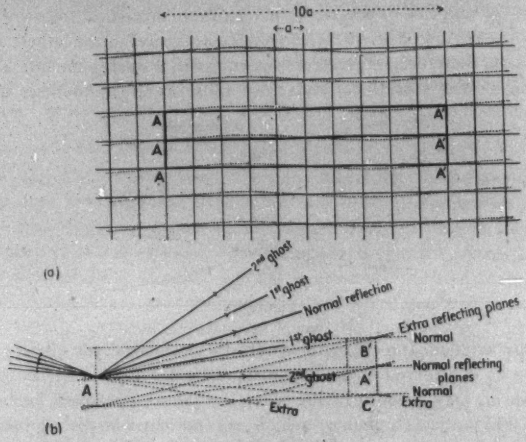


Figure 13.

(*a*) Showing super-lattice due to presence of transverse wave of length 10 *a*.
(*b*) Showing extra reflections from new planes introduced by super-lattice (angles exaggerated).

Now there are, of course, many such stationary waves to be considered, and these have various directions, wave-lengths and polarizations. Each imposes on the crystal a super-lattice and each atom in the crystal belongs simultaneously to all these super-lattices. Each super-lattice introduces a pair of extra reflecting points for every reciprocal-lattice point, and hence *each reciprocal-lattice point* (taking all the super-lattices into account) *will be surrounded by a cloud of weak extra reflecting power*, its own reflecting power being correspondingly reduced. Will the distribution of intensity of this cloud be spherical for all lattice points ? Only if the velocity (which is determined by the frequency) of an elastic wave of given wave-length and polarization is the same whatever its direction of propagation in the crystal. This condition is never fulfilled, even approximately,* as will be shown later.

Waves, whether longitudinal or transverse (or a mixture of both), travelling

* The assumption of such a condition has wrongly led Raman to reject the thermal theory as being inconsistent with experiment. Theorists have often, unfortunately, assumed this condition for simplification of the calculations.

along a given crystal direction in real space, give extra reflecting points *along that same direction* for each lattice point in reciprocal space, but the intensity of reflecting power along these extended directions depends not only on the frequencies but also upon the polarizations of the waves, that is, on the direction of the atomic movements relative to the various crystal planes. This introduces differences between different reciprocal-lattice points which will be described in more detail later.

The intensity of reflecting power at any point in the neighbourhood of a reciprocal-lattice point is also dependent upon the total angle of deflection 2θ. This angle enters into the intensity expression in a number of ways (see Born and Sarginson, 1941), some of which involve a *decrease* and others an *increase* of intensity with increasing 2θ. For instance, the polarization factor $(1+\cos^2 2\theta)/2$ and the atom-scattering factor f (which is dependent upon $\sin\theta/\lambda$), which are common both to Bragg and to extra reflections, involve a decrease of intensity with increasing 2θ. So does the modification of the atom-scattering factor due to the atomic vibrations, a factor which changes f into fe^{-M} where M is dependent upon $\sin\theta/\lambda$, absolute temperature T and the interatomic forces (Debye, 1914; Waller, 1925; Waller and James, 1928; James, Waller and Hartree, 1928). On the other hand, a given atomic oscillation will cause more spreading of reflecting power for planes of small than for those of large spacing, and this fact enters the intensity expression as a term $(1-\cos 2\theta)=2\sin^2\theta\sim\frac{1}{4}(n\lambda/d)^2$, where d is the spacing corresponding to the nearest lattice point.

The x-ray wave-length λ only influences the intensity indirectly, through θ and through the term $\sin\theta/\lambda$ which enters into the expression for the atom-scattering factor and its temperature modification.

The extra intensity is also very dependent upon the temperature T. As mentioned before, the amplitudes of the oscillations are influenced by temperature because of the increase of mean energy $h\nu\left(\frac{1}{2}+\frac{1}{e^{h\nu/kT}-1}\right)$ with T (for vibrations of low frequency the mean energy is kT), and the intensity is controlled by the mean-square amplitude in two ways: (1) directly, as a result of the actual atomic displacements; (2) indirectly, as an exponential modification of the atom-scattering factor (see last paragraph). Before the law of dependence upon temperature can be experimentally tested, however, it is necessary to know what range of frequencies is operative in giving any particular extra spot, and, therefore, we must consider in rather more detail the shape of the contours of equal reflecting power around any particular lattice point, and the dependence of extra intensity in the neighbourhood of the lattice point upon the nature of the crystal.

In order to do this we shall consider the simple case of a harmonic wave travelling along a main crystallographic direction, and determine the effect on the reflecting power in the neighbourhood of various reciprocal-lattice points. Leaving the variation with 2θ and T out of account, we know that

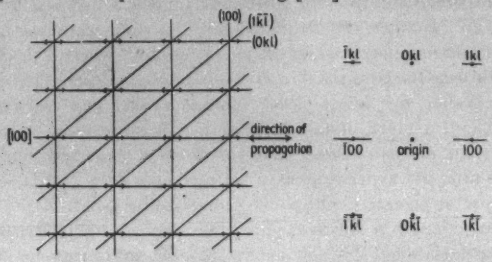
(1) Elastic waves propagated along a given direction in the crystal cause an extension of reflecting power of each reciprocal-lattice point along the direction of propagation. Each wave-length μ contributes to the reflecting

power at a definite point along this direction (or rather a pair of points, one on each side of the lattice point, which itself corresponds to waves for which $1/\mu = 0, 1/a, 2/a \ldots$.).

(2) The intensity of reflecting power at any given point depends on 1/(frequency)^2 of the contributing waves. This factor introduces both the wave-length μ and the elasticity of the crystal in respect of the atomic movement involved.

(3) The intensity also depends upon the square of the cosine of the angle between the radius vector of the given point in reciprocal space and the direction of the atomic movements (that is, upon the polarization of the waves).

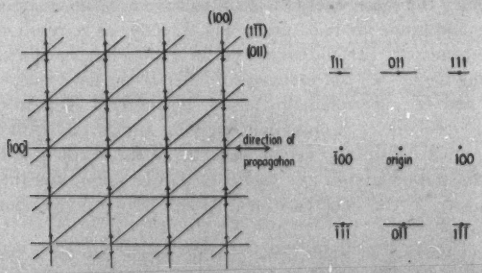
In figure 14 there is shown schematically a longitudinal wave travelling along the [100] direction of a cubic crystal. The extension of reflecting power for *each* reciprocal-lattice point will be along [100]. Since the atomic movements



(*a*) Real lattice, longitudinal vibration. (*b*) Reciprocal lattice, extension of reflections.

Figure 14.

take place along [100], that is, *parallel* to the (0*kl*) planes, the intensity of extra reflecting power for all (0*kl*) planes will be zero, whereas that for the (100) planes will be a maximum (since the atoms move *perpendicular* to the (100) planes).



(*a*) Real lattice, transverse vibration. (*b*) Reciprocal lattice, extension of reflections.

Figure 15.

For general planes (*hkl*), the intensity will be intermediate in value. Since the atomic movements only involve simple compression or expansion along a cube direction, the velocity of the wave is dependent upon c_{11}, in fact it equals

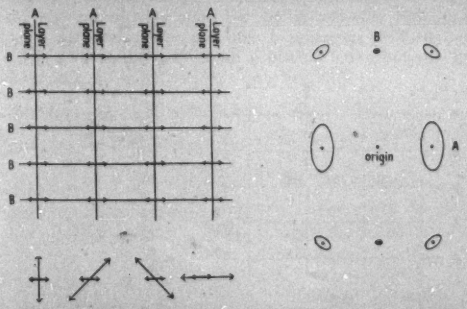
$\sqrt{(c_{11}/\rho)}.f(\mu)$, where ρ is the crystal density and $f(\mu)$ a function of the wavelength.

A transverse wave travelling along the same [100] direction (figure 15) will have quite a different effect on the reflecting power of the various planes. The atomic movements are now *parallel* to the (100) planes, and the reflection from those planes is therefore not affected. They are *perpendicular* to one of the (0*kl*) planes, say (011), and the reflecting power of (011) is therefore extended along the [100] direction. The atomic movements involve simple shear of the (100) planes, and the velocity of such a wave will be $\sqrt{(c_{44}/\rho)}.f(\mu)$. Since c_{44} is always less, and may be very much less, than c_{11}, the velocity of transverse waves is always less than that of longitudinal waves of equal length, along the cube directions of a cubic crystal.

By such simple considerations as these, it is possible to arrive at general conclusions concerning the extra reflections from "layer" and "chain" structures.

Layer structures

The atoms in the layer planes A of a structure such as graphite, hexamethylbenzene, etc., are more densely packed and more closely bound than in other crystal planes. Such planes are often cleavage planes, the forces between them are weak van der Waals forces, and can be easily disrupted to permit gliding, or even the introduction of foreign atoms. Layer structures are most compressible in a direction normal to the layer plane and bend most easily about directions in that plane. In other words, the atoms move most easily



Preferred modes of vibration have amplitudes normal to layer plane for all directions of propagation.

Reflecting regions in reciprocal lattice of a LAYER structure.

Figure 16.

in the direction of the normal to the layer plane. Waves polarized in this way will have the biggest amplitudes no matter what their directions of propagation, and, therefore, *the layer plane will show a maximum extension of reflecting power in every direction in reciprocal space*, and a maximum temperature change. The favoured direction of atomic movement is parallel to planes, such as B, which are normal to the layer plane, and such planes, therefore, will show a minimum extension of reflecting power in all directions.

This is fully borne out by observation. Laue photographs of layer structures are characterized by one very large, intense and persistent extra reflection, which must correspond to a huge spreading of reflecting power about the reciprocal-lattice point of the layer planes. Graphite, for instance, shows an enormous extra reflection for all observable orders from its cleavage plane, and these completely disappear at liquid-air temperatures, while all other planes give quite small extra reflections (plates 4 (*a*), 5 (*a*) and (*b*)).

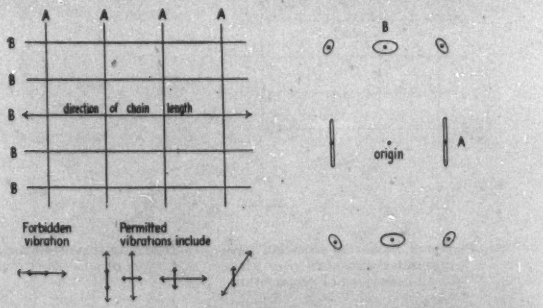
The " background " of the Bragg reflection from a layer plane will sometimes appear even on a rotation or Weissenberg photograph, although as a rule the exposure given to such a photograph is insufficient to show the background effects.

It is noteworthy that Hughes (1941), in determining the structure of melamine by means of a Fourier analysis, found it necessary to apply a differential temperature correction for structure factors of planes parallel or normal to the molecular planes of this layer structure. The spreading of reflecting power for planes nearly parallel to the molecular layers was sufficient to reduce the observed structure factors quite materially even at room temperatures. Raman and his colleagues (1941 Symposium in the *Proc. Ind. Acad. Sci.*) have observed that the extra reflections can be quite strong even for planes which have a relatively weak intrinsic reflecting power, provided that those planes are nearly parallel to the molecular layers. They instance this as being a proof that the optical vibrations are responsible for the extra reflections ; but it is, in fact, a consequence of the elastic vibration theory, since the amplitudes depend on the quasi-elastic interatomic forces, not on the static structure factor of the plane under consideration, and these forces are very anisotropic both for layer structures and for the chain structures which will be next considered. The misunderstanding has, of course, arisen from Raman's incorrect assumption that the elastic forces are equal in all directions for waves of all kinds.

The existence of a differential temperature effect means also that the relative intensities of Bragg and extra reflections may vary considerably with temperature for different crystal planes, as has been found (Kracek, Posnjak and Hendricks, 1931 ; Raman and Nilakantan, 1940).

Chain structures

Müller (1941) has shown that for long-chain compounds the compressibility along the length of the chain is several times smaller than that in directions at right angles. This means that longitudinal vibrations along the chain axis cannot take place. This prohibition does not affect the spreading of reflecting power about the points B, which will take place in all directions (the forbidden movements would have been parallel to the



Reflecting regions in reciprocal lattice of a CHAIN structure.

Figure 17.

planes B) ; but it means that there can be *no extension of reflecting power for points A along the chain direction*. The surfaces of equal reflecting power for A and for lattice points corresponding to planes nearly normal to the chain direction will be *discs*, while those for B and neighbouring lattice points will be more nearly spheroidal.

The extra spots corresponding to planes such as B will be large and more nearly circular (figure 18), while those corresponding to planes such as A will be fine lines perpendicular to the chain direction (figure 19). Sometimes it is possible to observe both types of spot on one Laue photograph (plate 4 (*b*)). Such photographs as these not only allow us to detect at once the presence of a chain structure, but show which planes are

normal to the chain direction and so form a useful subsidiary method of structure determination. In structures which consist of chains of lath-like molecules, the orientation of the

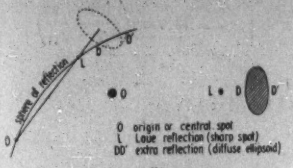


Figure 18.

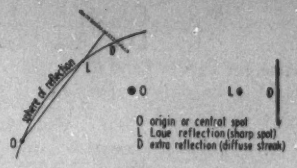


Figure 19.

molecules (although not their relative translations) can be settled entirely by observation of the extra reflections (Lonsdale, Robertson and Woodward 1941).

Cubic crystals

Although the general Waller formula is rather unmanageable, it can be expressed in a relatively simple way for cubic crystals of anisotropic elastic properties; this has been done by Zachariasen (1941) for some special cases and independently by Jahn (1942), whose general formula is now given * :

$$
\begin{aligned}
I \propto \frac{R^2}{r^2}\{&c_{44}^2 + L^2[c_{44}(c_{11}-c_{44})(m^2+n^2)+(c_{11}+c_{12})(c_{11}-c_{12}-2c_{44})m^2n^2]\\
&+M^2[c_{44}(c_{11}-c_{44})(n^2+l^2)+(c_{11}+c_{12})(c_{11}-c_{12}-2c_{44})n^2l^2]\\
&+N^2[c_{44}(c_{11}-c_{44})(l^2+m^2)+(c_{11}+c_{12})(c_{11}-c_{12}-2c_{44})l^2m^2]\\
&-2MNmn(c_{12}+c_{44})[c_{44}+(c_{11}-c_{12}-2c_{44})l^2]\\
&-2NLnl(c_{12}+c_{44})[c_{44}+(c_{11}-c_{12}-2c_{44})m^2]\\
&-2LMlm(c_{12}+c_{44})[c_{44}+(c_{11}-c_{12}-2c_{44})n^2]\}\div\\
&\{c_{11}c_{44}^2+c_{44}(c_{11}+c_{12})(c_{11}-c_{12}-2c_{44})(l^2m^2+m^2n^2+n^2l^2)+\\
&\qquad(c_{11}+2c_{12}+c_{44})(c_{11}-c_{12}-2c_{44})^2l^2m^2n^2\}.
\end{aligned}
$$

I is the intensity of extra reflecting power at a distance r in the direction $[l, m, n]$ from a reciprocal-lattice point P, distant R from the origin of reciprocal space,

Figure 20.

the direction cosines of R being $[L, M, N]$; c_{11}, c_{12}, c_{44} are the elastic constants of a cubic crystal, in terms of which the compressibility is $(c_{11}+2c_{12})/3$ and the

* This formula applies to a cubic crystal of any lattice, simple, face-centred or body-centred, if the optical vibrations are neglected.

shear constant c_{44}. The crystal is said to be elastically isotropic if $c_{11}-c_{12}=2c_{44}$, and in that case the formula reduces to

$$I \propto \frac{R^2}{r^2}\left\{\Sigma L^2\left[\frac{1}{c_{11}}+\left(\frac{1}{c_{44}}-\frac{1}{c_{11}}\right)(m^2+n^2)\right]-2\Sigma MNmn\left(\frac{1}{c_{44}}-\frac{1}{c_{11}}\right)\right\}.$$

Hence, for a given I and R,

$$r^2 \propto \frac{1}{c_{11}}+\left(\frac{1}{c_{44}}-\frac{1}{c_{11}}\right)[1-(Ll+Mm+Nn)^2]$$
$$\propto \frac{\cos^2\theta}{c_{11}}+\frac{\sin^2\theta}{c_{44}},$$

where θ is the angle between the vectors R and r.

It will readily be seen that, for a given value of R and I, r^2 can never be constant unless $c_{11}=-c_{12}=c_{44}$ (condition for spherical spread of reflecting power). In that case, however, $c_{11}+2c_{12}=-c_{44}$, involving a negative compressibility or a negative shear constant, either of which is absurd. The surfaces of equal reflecting power (isodiffusion surfaces) cannot be spherical. In fact, even in the unusual event of a negative c_{12}, the highest value that c_{44} can have in an isotropic cubic crystal is $3c_{11}/4$; if c_{12} is positive then $c_{44}<c_{11}/2$ (Jahn and Lonsdale, 1942).

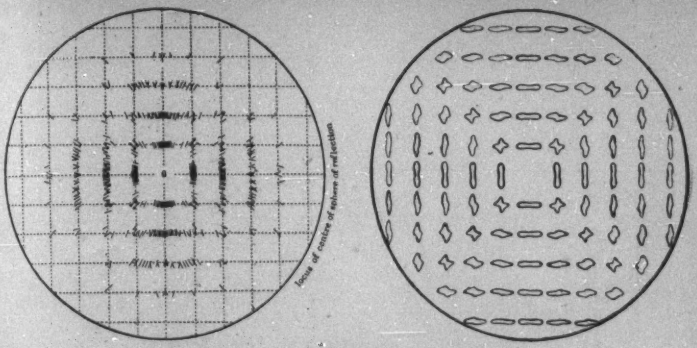
The presence of R^2 in the formula would make it appear that the intensity of extra reflection must increase rapidly as the spacing of the planes decreases. R^2 is, in fact, the term $(1-\cos 2\theta)$, which was previously mentioned as leading to an increase of intensity with increasing θ. It must be remembered that the Jahn formula given above does not introduce those factors (polarization factor, atom-scattering factor, etc.) which cause a decrease of intensity with increasing θ. The combined effect of such factors in practice is (as Laval has shown, and as may easily be observed) that the integrated extra reflections do in general fall off in intensity with increasing angle of deviation, but not so rapidly as the Bragg reflections. In the subsequent discussion, therefore, R^2 will be omitted.

Many interesting consequences of the formula have been given by Jahn, but perhaps one of the most instructive is its application to such crystals as KCl (for which $c_{11}-c_{12}>2c_{44}$) or to metals such as sodium or lead (for which $c_{11}-c_{12}<2c_{44}$). There are various ways of comparing formula and photograph, but in practice the intermediate use of the reciprocal lattice is almost indispensable. From the formula it is possible, by substituting values of c_{11}, c_{12}, c_{44}, L, M, N and l, m, n to plot the values of r corresponding to a constant I for each reciprocal lattice point (*isodiffusion surfaces*), or to plot the values of I corresponding to a constant r. This gives a distribution of reflecting power about each reciprocal-lattice point which, as mentioned before, always involves a maximum extra reflecting power along certain reciprocal-lattice *planes* or *axes*, but in which the relative extensions of reflecting power along those directions vary from one lattice point to another.

By calculating back from the photographs to the reciprocal lattice (analytically or geometrically), it is possible either

(1) to compare the experimentally observed extensions of reflecting power about each point, plotted from a complete series of photographs, with the picture given by the formula, as in figures 21 (*a*) and (*b*) ; or

(2) to compare the positions and intensities of the extra reflections on one Laue photograph at a time, with the intersections of the corresponding sphere of reflection with the theoretical (three-dimensional) diagram. Using the latter



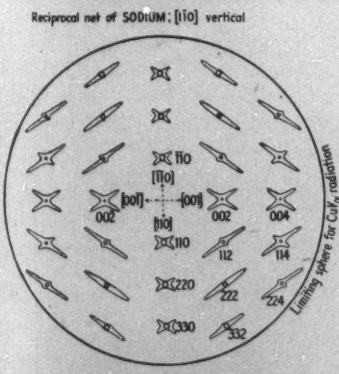
(*a*) (*b*)

Fig. 21.

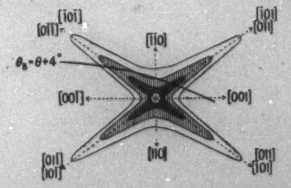
(Reproduced by courtesy of the Council of the Royal Society.)

(*a*) KCl ; Ag Kα : reciprocal net showing observed positions of extra spots on central layer-line of Laue photographs taken with cube axis of crystal vertical.

(*b*) KCl ; Ag Kα : reciprocal net showing values of I (r constant) for [$hk0$] lattice points, calculated from the Jahn formula. The decrease of intensity with scattering angle is indicated by decreasing line intensity.



Showing intensity distributions (projected on (1$\bar{1}$0) plane) for various lattice points. Intensity of [1$\bar{1}$0] peak indicated by circles. Distances along other directions are proportional to I of Jahn's formula (r constant).



Enlargement of 002 reflecting region showing trace of sphere of reflection for $\theta=\theta_B+4°$ (the four peaks shown are pointing up out of plane of paper at 30° and are accompanied by four similar peaks pointing down at 30°).

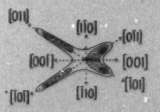


Diagram showing section of 002 reflecting region by sphere of reflection (compare plate 6 (*a*)).

Figure 22.

method, Lonsdale and Smith (1941 d, 1942 a) have shown that the observed extra reflections for Na, Pb and W single crystals correspond in detail with the predictions of the Jahn formula. To take one example (figure 22, plate 6 (*a*))

Table 1. Values of I from Jahn's formula (r constant)

$LMN\rightarrow$ / $lmn\downarrow$	Na			Pb			W			KCl		
	001	$\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}0$	$\frac{1}{\sqrt{3}}\frac{1}{\sqrt{3}}\frac{1}{\sqrt{3}}$	001	$\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}0$	$\frac{1}{\sqrt{3}}\frac{1}{\sqrt{3}}\frac{1}{\sqrt{3}}$	001	$\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}0$	$\frac{1}{\sqrt{3}}\frac{1}{\sqrt{3}}\frac{1}{\sqrt{3}}$	001	$\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}0$	$\frac{1}{\sqrt{3}}\frac{1}{\sqrt{3}}\frac{1}{\sqrt{3}}$
100	24	22	22	7	5	5	0·66	0·43	0·50	15	9	11
010	24	22	22	7	5	5	0·66	0·43	0·50	15	9	11
001	19	24	22	2	7	5	0·20	0·66	0·50	3	15	11
$\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}0$	24	12	16	7	2	3	0·66	0·20	0·35	15	4	7
$\frac{1}{\sqrt{2}}\frac{\bar{1}}{\sqrt{2}}0$	24	165	118	7	27	20	0·66	0·66	0·66	15	6	9
$0\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}$	86	56	16	14	11	3	0·43	0·54	0·35	5	10	7
$0\frac{1}{\sqrt{2}}\frac{\bar{1}}{\sqrt{2}}$	86	56	118	14	11	20	0·43	0·54	0·66	5	10	9
$\frac{1}{\sqrt{2}}0\frac{1}{\sqrt{2}}$	86	56	16	14	11	3	0·43	0·54	0·35	5	10	7
$\frac{\bar{1}}{\sqrt{2}}0\frac{1}{\sqrt{2}}$	86	56	118	14	11	20	0·43	0·54	0·66	5	10	9
$\frac{1}{\sqrt{3}}\frac{1}{\sqrt{3}}\frac{1}{\sqrt{3}}$	30	20	10	10	6	2	0·50	0·35	0·20	6	5	4
$\frac{\bar{1}}{\sqrt{3}}\frac{1}{\sqrt{3}}\frac{1}{\sqrt{3}}$	30	41	37	10	14	12	0·50	0·66	0·61	6	8	7
$\frac{1}{\sqrt{3}}\frac{\bar{1}}{\sqrt{3}}\frac{1}{\sqrt{3}}$	30	41	37	10	14	12	0·50	0·66	0·61	6	8	7
$\frac{1}{\sqrt{3}}\frac{1}{\sqrt{3}}\frac{\bar{1}}{\sqrt{3}}$	30	20	37	10	6	12	0·50	0·35	0·61	6	5	7
(At 290° K.) $10^{11}\times$	c_{11} 0·521	c_{12} 0·400	c_{44} 0·410	c_{11} 4·77	c_{12} 4·03	c_{44} 1·44	c_{11} 50·7	c_{12} 20·2	c_{44} 15·2	c_{11} 3·88	c_{12} 0·64	c_{44} 0·65

Table 2. Observed and calculated extra intensities for sodium

(*hkl*)	±[*pqr*]	[100]	[010]	[001]	[110]	[1$\bar{1}$0]	[011]	[01$\bar{1}$]	[101]	[$\bar{1}$01]
(002)		— (24)	— (24)	— (19)	— (24)	— (24)	M.S. (86)	M.S. (86)	M.S. (86)	M.S. (86)
(110)		— (22)	— (22)	— (24)	— (12)	V.S. (165)	M. (56)	M. (56)	M. (56)	M. (56)
(112)		— (24)	— (24)	— (21)	— (20)	M. (71)	W. (30)	S. (133)	W. (30)	S. (133)
(222)		— (22)	— (22)	— (22)	— (16)	S. (118)	— (16)	S. (118)	— (16)	S. (118)

the (002) extra reflection for Na, when the [1$\bar{1}$0] axis is vertical and the angle of incidence is $\theta_B + 4$ (25°·3 for CuKα), consists of what looks like *a pair of scissors*, but *with no hinge* of appreciable intensity. This corresponds to the intersection, by the sphere of reflection, of intensity spikes along directions [$\bar{1}$0$\bar{1}$] [0$\bar{1}$1] (blades of scissors) and [$\bar{1}$01] [01$\bar{1}$] (handles of scissors). There is no hinge because there is no intensity spike along [$\bar{1}\bar{1}$0]. Other photographs show that for the (002) reciprocal-lattice point there are no intensity spikes along [1$\bar{1}$0] [$\bar{1}$10], although for the (110) point the intensity spikes along [1$\bar{1}$0] [$\bar{1}$10] are particularly strong (plate 6 (*b*)). Others, again, illustrate the fact that for the (222) point there are no intensity spikes along [101] [011] [110] [$\bar{1}$0$\bar{1}$] [0$\bar{1}$1] or [$\bar{1}$10], although along the remaining six diagonal directions they are strong. Tables 1 and 2 show how figures 21 and 22 are deduced from the Jahn formula, and

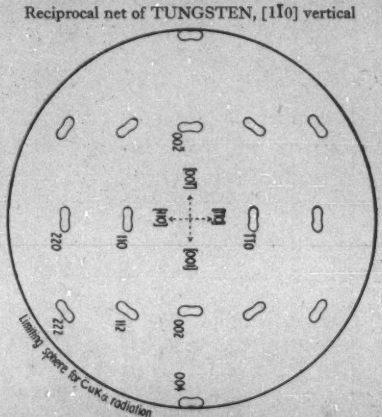


Figure 23. Relative values of *I* are shown on a scale 80 times larger than those shown in figure 22 for sodium. (Compare table 1.)

how the absence of certain spots and streaks (which was inexplicable in terms of the simple diffraction theory) is strictly in accordance with the formula, which predicts that the intensity spikes along those very directions shall be absent or weak.

Lonsdale and Smith have found that lead (plate 7) also gives extra reflections corresponding to intensity spikes along the various [110] directions, which are similar to, although less extended than, those found for sodium, and this in spite of the fact that sodium has a body-centred cubic structure, whereas lead has a face-centred cubic structure. Table 1 shows that this similarity is predicted by the Jahn formula, which, since it neglects optical vibrations, gives similar results for cubic crystals of all classes *provided that they are elastically similar*. Sodium and lead are both elastically anisotropic in the same sense ($c_{11} - c_{12} < 2c_{44}$), and their elastic constants are small. On the other hand, tungsten single crystals, although similar in crystal structure to sodium, give quite different extra reflections. Those of sodium (and lead) are intense, large and detailed in structure, and persistent over a wide range of angles of incidence; those of tungsten are weak,

small, elliptical, and disappear very quickly as the angle of setting departs from the Bragg angle for each plane in turn. This is because the elastic constants for tungsten are large and isotropic ($c_{11}-c_{12}=2c_{44}$) and lead, therefore, to quite a different intensity distribution (table 1 or figure 23) around the reciprocal lattice points from that found for soft, anisotropic metals.

It is possible to see the relation of the sheets of atoms postulated in the simple diffraction theory to the actual state of affairs in the crystal when it is realized that normal to the propagation directions of the elastic waves of lowest velocity there will, indeed, be sheets of atoms scattering more nearly in phase with each other than with atoms in other directions; but the phase relationships between successive sheets cannot be ignored, since they are not by any means random. It is here that the simple diffraction theory breaks down, in that it does not introduce any physical property of the crystal which shall decide either *which sheets shall be chosen, or what are the phase-relationships between successive sheets.*

Effects due to strain, intrinsic or mechanical

It has been pointed out that, in addition to the extra reflections referred to above, which appear with equal intensity under similar conditions for any crystal of the same sort, there are sometimes extra reflections of quite another kind, which are structure-sensitive, but not temperature-sensitive. Although these do not come under the subject of this lecture, it is as well to refer to them, since they may be misleading. Such extra reflections, which are usually found on photographs of crystals having cleaved, ground or fractured surfaces, and are particularly common in the case of metals, are almost certainly due to the disordering of the lattice in one or more directions, by strain. Such effects the simple diffraction theory is adequate to deal with. In the case of a photographic survey they are unlikely to cause confusion because their sharpness and structure-sensitiveness distinguish them from the extra reflections due to the heat motions. In methods involving ionization measurements they are not so obviously distinguishable (Kirkpatrick, 1941 ; Teague, 1941 ; Lonsdale and Smith, 1941).

Diamond

This crystal will be considered separately because of its peculiarities, which as yet have received no adequate explanation. The elastic constants of diamond are not yet fully known, but they are certainly very large, and it is unlikely that they are very anisotropic. (The compressibility is $\sim 6\cdot10^{12}$ dynes/cm^2 (Adams, 1921, Williamson, 1922), and Young's modulus in the octahedral plane is given as $5\cdot5\,.\,10^{12}$ dynes/cm^2 by Pisharoty (1940).) The extra reflections to be expected on account of the elastic vibrations will therefore be single diffuse spots, elliptical in shape, which will fade out quickly as the angle of setting departs from the Bragg angle. Such reflections have been found for all observable planes of all the diamonds examined; they disappear almost completely at liquid-air temperatures ($-180°$ c.) and are increased considerably in intensity when the temperature is raised to 750° c. They correspond to a small ellipsoidal spreading of reflecting power about the reciprocal-lattice points. These extra reflections have been called *primary reflections* because some diamonds also show *secondary extra reflections* of a totally different character (Lonsdale and Smith, 1941 c). It was to these secondary reflections that Raman and Nilakantan drew attention in announcing their new theory. The secondary reflections are relatively sharp and are only slightly, if at all, temperature-sensitive. They are, however, very structure-sensitive, being given in varying intensity by normal (type I) diamonds,

but not at all by the rare diamonds classed as being of type II (plate 5 (*c*) and (*d*)) (Robertson, Fox and Martin, 1934; Lonsdale, 1942). Normal diamonds, although monolithic, are generally believed to be in a state of internal strain, whereas in the rarer type II diamonds it is supposed that the strain has been relieved by the breaking up of the diamond into a mosaic of perfect crystallites. The secondary reflections found for {111} planes correspond to a sharply defined extension of reflecting power along all the cube directions. This extension leads to an interesting breakdown of Friedel's law; the reflection from a (111) plane changes when the plane is rotated through 180°, relative to the incident beam, that is, when the angle of incidence changes from θ_B to $-\theta_B$. This is because the extension of reflecting power is not symmetrical about the radius vector of the (111) reciprocal-lattice point. The extension along the cube directions about the {111} points in reciprocal space is *geometrically* accounted for either by the existence of sheets of atoms scattering in phase, parallel to the cube planes, but with a randomness of phase in other directions (W. H. Bragg, 1941), or by the existence of sharply defined lattice waves propagated only along cube directions, the atomic movements being normal or nearly normal to the {111} planes (Pisharoty, 1941; Lonsdale and Smith, 1941; Sirkar and Bishui, 1941; Lonsdale, 1942). Neither of these hypotheses, however, satisfactorily accounts for the fact that the extension of reflecting power about the (220) and (113) planes is not along *all* the cube directions, but only along [100] and [010]; the [001] intensity spike is missing for those two planes, but is present for the (331) plane. The (331) and (004) planes show no intensity spikes along [010] and [100]. The absence of certain intensity spikes could have been accounted for in terms of polarization of certain lattice waves, but the particular combinations that are found do not fit in with each other on any such hypothesis; while the idea of simple two-dimensional sheets of atoms does not permit the absence of any intensity spikes at all.

Bearing these unexplained experimental facts in mind, it is interesting to consider the third theory that has been advanced.

§ 6. RAMAN THEORY

Raman had rejected the Faxén-Waller theory on the erroneous assumption that it inevitably leads to a very weak spherical distribution of intensity around each reciprocal-lattice point (including the origin) which is proportional to the Bragg intensity for each point.

He has suggested instead that the vibrations responsible for the extra reflections must be monochromatic vibrations in the optical branches, of frequency 10^{12} to 10^{14} sec^{-1}, which are, he suggests, excited by the incident x rays. In order to account for the secondary reflections from (111) diamond planes (the observations made by Raman and Nilakantan do not appear to have included primary reflections, nor reflections from any other planes of diamond) he suggests that the 1332 cm^{-1} vibration, in which neighbouring carbon atoms vibrate against each other normal to the (111) planes, is excited by the x rays all over the crystal simultaneously, but that there are small changes of phase from one unit cell to the next which are of such a nature that "phase-waves" are propagated along the cube directions. These phase-waves, whose frequency is determined by the frequency of the characteristic vibration, reflect the x rays coherently,

with a change of frequency equal to that of the excited vibration. (Since the excited vibration is of a frequency far smaller than that of the incident radiation, this change would be quite impossible to measure. A similar change is given by the Faxén-Waller theory, as was first pointed out by Laue, but it is of little experimental significance, except in so far as it leads to the essential incoherence, and therefore diffuseness, of the extra reflections.)

Raman gives for the law of temperature variation of the vibration energy a factor $\frac{e^{h\nu/kT}+1}{e^{h\nu/kT}-1}$, which is of the same form as that given in the Faxén-Waller theory, although his method of deduction is not clear. There is this important difference in practical application, however: that whereas in the Raman theory only the excited monochromatic frequencies should be used in this formula, according to the Faxén-Waller theory the frequencies or range of frequencies which must be considered are those which give the particular extra spots under observation.

Venkateswaran (1941) has made a few measurements of the variation of intensity of extra reflections with temperature, on carborundum, $NaNO_3$, NaCl, and pentaerythritol, and has suggested that they may be fitted to the formula $I_T \propto \frac{e^{h\nu/kT}+1}{e^{h\nu/kT}-1}$ if ν corresponds to about 800 cm.$^{-1}$ for carborundum, 200 cm.$^{-1}$ for $NaNO_3$, 160 cm.$^{-1}$ for NaCl and <100 cm.$^{-1}$ for pentaerythritol. These frequencies he identifies with known *Reststrahlen* or Raman frequencies. His experiments and deductions may be criticized on the following grounds:

(1) For $NaNO_3$ and for $C(CH_2OH)_4$ he has only two measurements, one at 90° K. and another at 300° K. These, being relative intensities, cannot be used to determine any curve uniquely. Baltzer (1941), for instance, has obtained relative intensity measurements for NaCl crystals at 300° A. and 100° A., which are numerically in close agreement with the measurements of Venkateswaran, but he has fitted them to the formula $I_{100} = I_{300}(1 - e^{-2M})$ given by Jauncey, Harvey and Woo (1931, 1932).

(2) He has neglected the effect of temperature in modifying the atom-scattering factor. The spread of electron density due to atomic vibration results in a decrease of the effective atom-scattering factor, which is greater the higher the temperature, the smaller the spacing and the larger the amplitude of vibration. By measurement of this factor for Bragg reflections of NaCl, Waller and James (1928) have been able to show that the root-mean-square amplitude of the Cl atoms is 0·217 A. and of the Na atoms 0·242 A., both at 290° K. For the 200 and 220 reflections (which Venkateswaran presumably measured) this corresponds to a decrease of intensity of 16 and 28 per cent. respectively, at 300° K., as compared with 90° K. This modification of the f-factor to fe^{-M} (where M is a function of temperature, total angle of deflection, wave-length and the interatomic forces) applies also to the extra reflections (Born and Sarginson, 1941), and it is important to notice that it results in a decrease of intensity with increasing temperature. Allowing for this factor, the real increase in the intensity due to the energy factor $\frac{e^{h\nu/kT}+1}{e^{h\nu/kT}-1}$ will be considerably larger than the measured increase, and the deduced value of ν will be considerably smaller. In the case of NaCl, which is the only

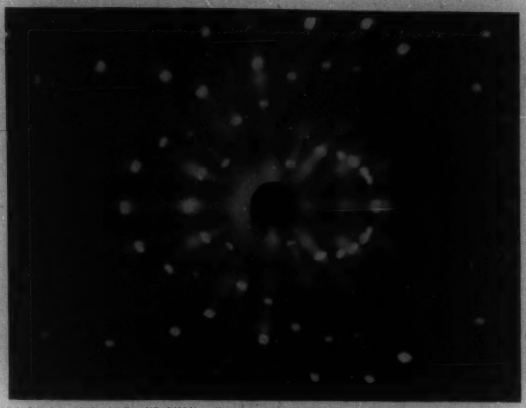
one of the four compounds for which a numerical estimate of the necessary correction is available, the appropriate value of ν would correspond to about 100 $cm.^{-1}$ rather than 160 $cm.^{-1}$. This is, in fact, *below the range of optical frequencies for NaCl* (Kellermann, 1940). It corresponds to an acoustical frequency $\nu = 3 \cdot 10^{12}$ of rather short wave-length.

(3) In order to measure the intensity of the extra reflections at all, Venkateswaran has had to choose spots which are separated from neighbouring Laue spots by a region of low background intensity. This means that his measurements are necessarily made on extra reflections of fairly large wave-vector, that is, due to vibrations of fairly short wave-length. For instance, in the case of NaCl, it may be seen *by a geometrical construction* that the vibrations corresponding to the 200 and 220 extra reflections on his photographs are of wave-lengths of only about 22·5 A. and 12 A. respectively. Such waves must have relatively high frequencies in any case. All that Venkateswaran's experiments did in fact show was that the frequencies corresponding to relatively short waves would be of decreasing order of magnitude for SiC, $NaNO_3$, NaCl and $C(CH_2OH)_4$, a result which is fully in accordance with the Faxén-Waller theory, since that is the order of decreasing strength of quasi-elastic forces in the crystals.

Raman has argued that the X-ray diffraction due to the elastic waves would be proportional to N, the number of unit cells in the crystal; but that that due to excited characteristic waves would be proportional to N^2, and, therefore, of the same order as that of the normal Bragg reflections. There seems here to be a misunderstanding of ordinary diffraction theory. The integrated Bragg reflection from a small crystal is certainly proportional to $N_0^2 \delta V$ (*International Tables for Crystal Structure Determination*, **2**, 562 (1935)), but in this case N_0 is the number of unit cells per unit volume and N_0^2 is a constant for any given compound. The volume of the small crystal, δV, is proportional to the number of unit cells in the crystal, and, therefore, *the integrated intensity of the Bragg reflection*—like that of the extra reflections due to elastic vibrations—*is proportional to the number of unit cells in the crystal, N*. All the experiments carried out by Raman and his colleagues to prove that the Bragg and extra reflections depend in the same way upon the crystal (or irradiated) volume simply confirm the Faxén-Waller theory, because in all of them it is integrated intensities that are measured or estimated, not the intensity at a point.

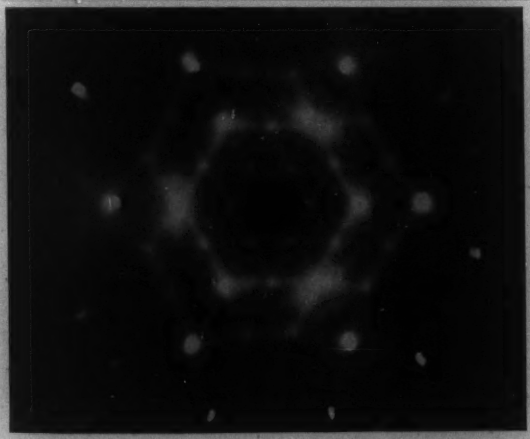
From the point of view of the accepted theory of lattice dynamics (due to Born and his collaborators) there is no justification for Raman's differentiation between the acoustical and optical vibrations; but Raman rejects the accepted theory and, in particular, he challenges the Born theory of the cyclic lattice. This point is dealt with in a forthcoming paper by Professor Born *, and need not be further considered here. It must be emphasized, however, that from the experimental side there is no evidence to show that the extra reflections due to the optical branches of the frequency spectrum will be of a higher order of intensity than those due to the acoustical branches. The relative intensities are simply controlled, as previously explained, by the relative frequencies, being, in fact, much smaller for the optical vibrations on account of their higher frequencies. In order to overcome this difficulty Raman makes assumptions

* Now published (this part, p. 362).



(*a*)

Sylvine (KCl), showing sharp Laue spots, diffuse extra spots and vertical streaks due to Ag characteristic radiation, and diffuse radial streaks due to white radiation.



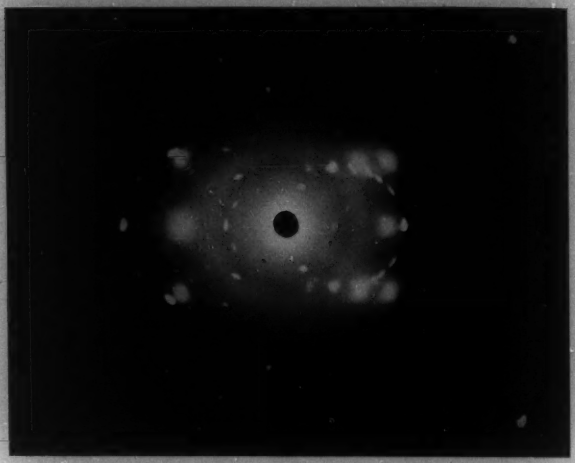
(*Reproduced by courtesy of the Council of the Royal Society*)

(*b*)

Benzil. Laue photograph taken with monochromatized Cu radiation. No radial streaks, very little background near centre, but strong extra spots and streaks corresponding to intersection of sphere of reflection with certain reciprocal-lattice axes and planes. 2-hr. exposure.

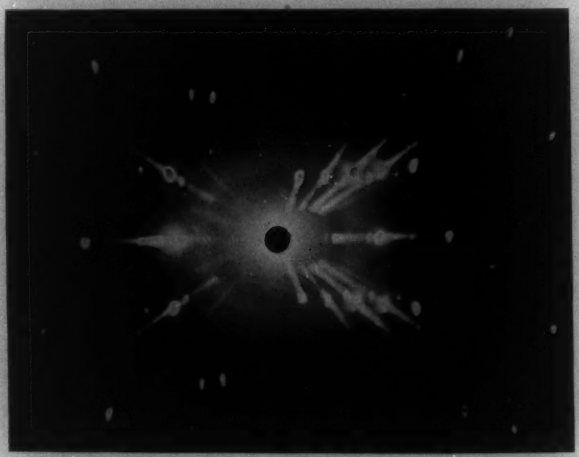
Plate 1.

To face page 342



(*a*)

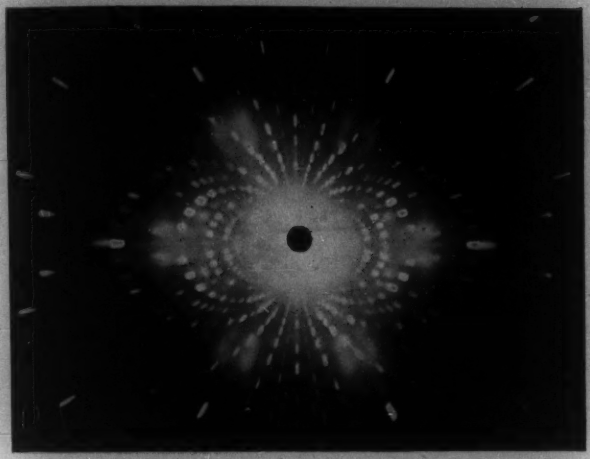
Diphenyldiacetylene; Cu radiation, partly filtered; Laue photograph (crystal stationary), 10-min. exposure. Compare positions of diffuse spots with oscillation spots in (*b*).



(*b*)

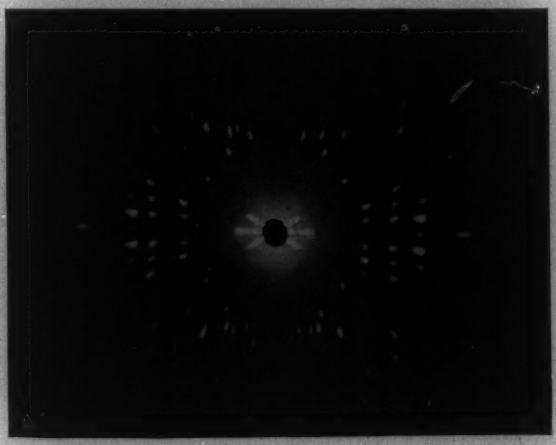
As in (*a*), but crystal oscillating; 10-min. exposure, showing strong "white" radiation streaks and diffuse background to some Bragg spots. (Cu radiation contains some tungsten lines.)

Plate 2.



(*a*)

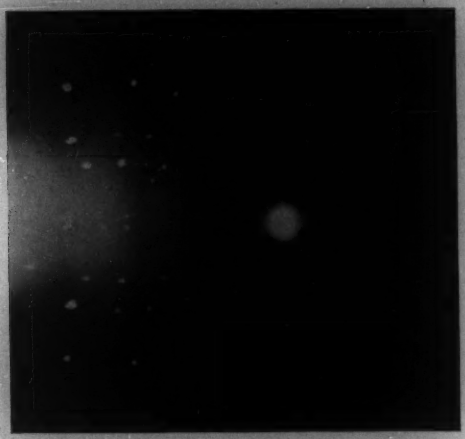
s-Triphenylbenzene. This orthorhombic crystal is composed of pseudo-trigonal molecules arranged in approximately parallel orientations. The extra reflections show the pseudo-hexagonal nature of the elastic forces. (Filtered Cu radiation, 20 min.)



(*b*)

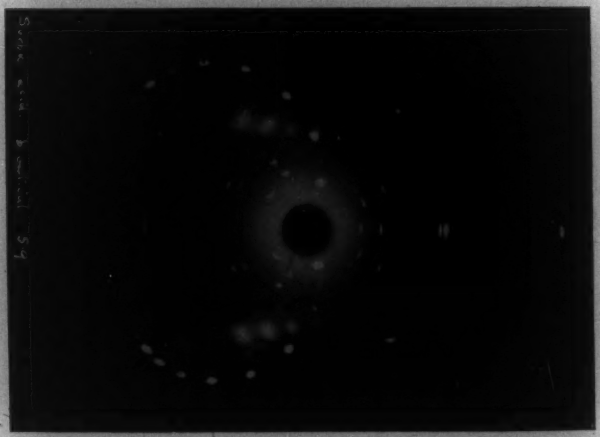
15° oscillation photograph corresponding to above setting of crystal. A careful comparison of these two photographs shows clearly that the intensities of the extra reflections are not necessarily proportional to those of the Bragg reflections. (Filtered Cu radiation, 4 min.)

Plate 3.



(*a*)

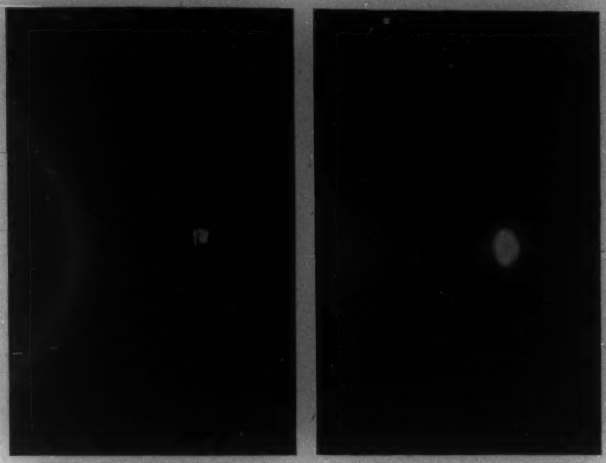
Typical *layer structure*: graphite 006 reflection at room temperature. Cu radiation. One large extra reflection.



(*b*)

Typical *chain structure*: sorbic acid. Streaky extra reflections correspond to planes nearly normal to chain axis; intense elliptical extra reflections correspond to planes nearly parallel to plane of molecules.

Plate 4.

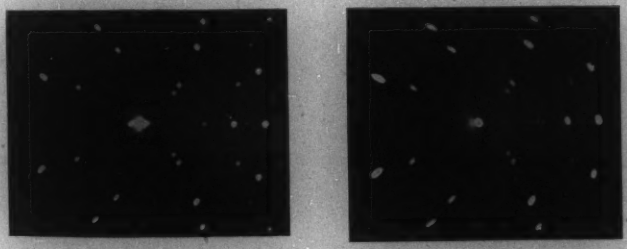


(*a*) (*b*)

(*a*) Graphite 004 reflection on Laue photographs at −180° C.
(*b*) „ „ „ „ at 25° C.,
showing disappearance of diffuse reflection at low temperatures.

Diamonds

Type I (normal) Type II (rare)

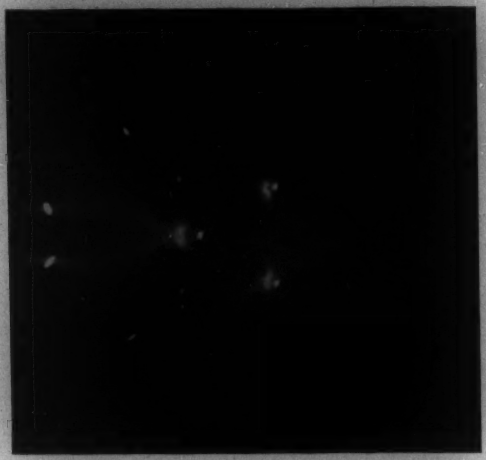


(*c*) (*d*)

(*c*) Diamond type I. The triangles of secondary extra spots associated with the 11$\bar{1}$ Laue reflection are given by FeKα (strong) and FeKβ (weak) radiations respectively.

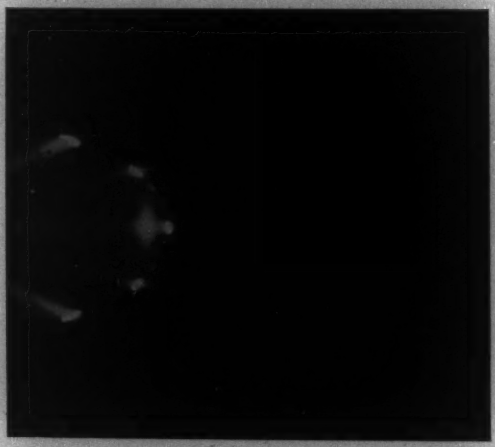
(*d*) Diamond type II. Similar crystal orientation. Only a single primary extra spot, due to FeKα radiation, is to be seen just by the 11$\bar{1}$ Laue reflection.

Plate 5.



(*a*)

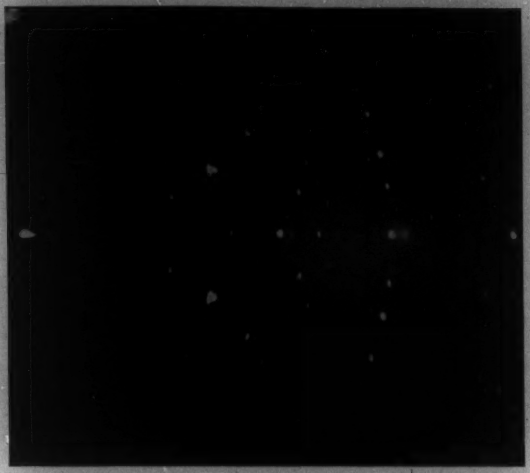
Sodium : Cu radiation, showing 002 extra reflection shaped like a pair of scissors. Note relative weakness of hinge of scissors and presence of strong non-radial streaks.



(*b*)

Sodium : Cu radiation, 110 extra reflection, showing strong vertical streak through close group of four spots forming square. (These four spots are clearly resolved in the original film, but detail has been lost in the reproduction.)

Plate 6.



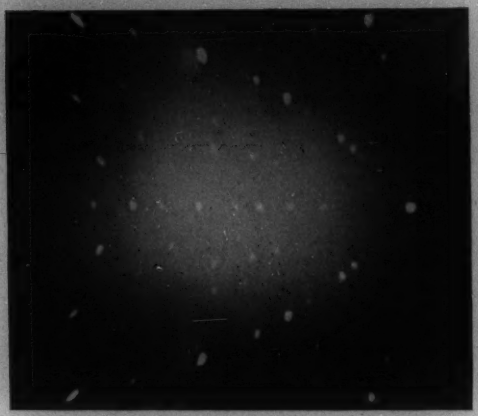
(*a*)

Lead: Cu radiation; Laue photograph at −180° c.; cube axis vertical; film parallel to incident beam; extra reflections much weaker than in (*b*), but many more Laue spots present.

(*b*)

Lead: Laue photograph at room temperature, showing strong extra reflections, which are very persistent as crystal is moved out of position. Exposure, 15 min. at 3·0 cm. in both photographs.

Plate 7.



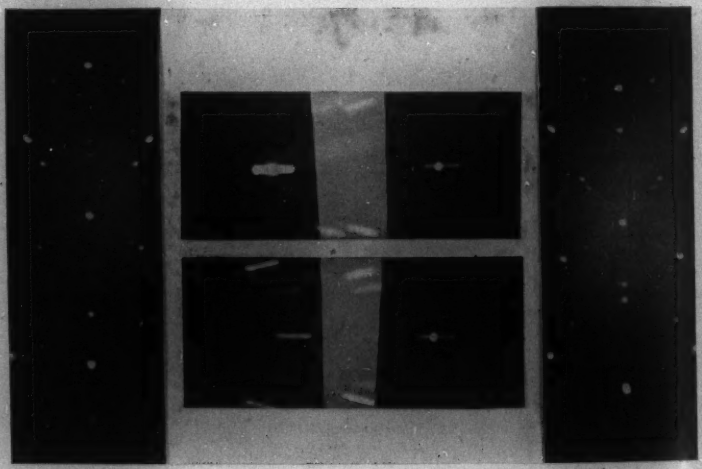
(*a*)

(*b*)

(*a*) Type I diamond, showing 202 reflection with large primary diffuse spot and sharp secondary spot corresponding to intersection of sphere of reflection with [001] horn. No secondary spot corresponding to a [010] horn (the [100] spot would not be observable in this orientation). Similarly, 022 reflection gives only [001] secondary spot, not [100].

(*b*) Type I diamond, showing 111, 202 and 022 reflections (last two in Bragg positions).

(*d*)



(*c*) (*e*) (*f*)

Type I diamond.

(*c*) $22\bar{2}$ Laue reflection ($\theta_{Bragg} - 1°$), showing no secondary detail.

(*d*) $11\bar{1}$ oscillation, showing secondary streaks in background, compared with $22\bar{2}$ oscillation (same exposure time and development), showing no streaks except that due to white radiation.

(*e*) Oscillation through 200 position, showing no characteristic reflection, compared with $22\bar{2}$ oscillation under similar conditions.

(*f*) 222 Laue reflection ($\theta_{Bragg} - 3°$) showing no secondary detail.

which, as Born has pointed out, contradict the elementary laws both of classical and of quantum mechanics, and lay a quite unjustifiable emphasis upon the optical range of frequencies.

Forbidden reflections

The distinctive feature of the Raman theory is, of course, the suggestion that the vibration energy is derived from the incident x rays. The possibility of an excitation of characteristic vibrations by x-ray energy was considered by Ott in 1935, and has recently been reconsidered by Born, both of whom have come to the conclusion that such excitation may certainly take place, but that the x-ray interference effects due to such high-frequency vibrations will be negligible compared with those due to the low-frequency elastic vibrations, since the intensity of x-ray diffraction varies inversely as the frequency^2. For the acoustical vibrations, $\overline{\nu^2}$ is a function of μ which becomes zero when $\mu = \infty$, a, $a/2$, $a/3$ .... (a being the lattice constant); for the optical vibrations ν^2 is never

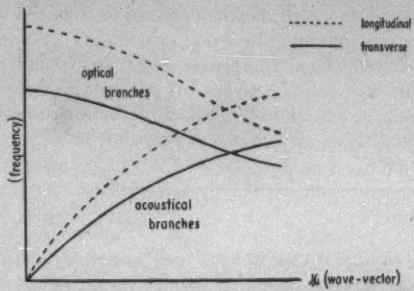


Figure 24.

zero, but has minimum values for $\mu = 2a$, $2a/3$, $2a/5$ .... (Born, 1942). These minimum values may be lower than some of the high-frequency acoustical vibrations, but they occur at the edge of the Brillouin zone and correspond to extra reflections about half-way between neighbouring reciprocal-lattice points. It is only in these positions that the infra-red vibrations may be observable in some cases. Observations in this region are therefore of considerable interest.

Ott (1935; footnote to p. 190) suggested that it was possible that a "Raman effect" might be observable in, say, the 222 reflection position for diamond, and might possibly account for the well-known "forbidden" reflection found in that position. This suggestion has been revived by Raman and by one of his collaborators, P. Rama Pisharoty (1941), who has given a list of "permitted" and "forbidden" Bragg and extra reflections in diamond, on the basis of a theory which assumes the excitation of characteristic 1332 cm^{-1} vibrations perpendicular to one set of (111) planes only. This procedure is most arbitrary, for whatever oscillations take place are certainly symmetrical with respect to all the {111} planes, all of which show similar extra reflections. It is also misleading, for vibrations normal to (111) planes would certainly have a different component relative to (220) planes, say, from those normal to (111); but this he has not taken into account. He claims that there should be no extra reflections

for (220) planes of intensity at all comparable with those found for (111), and states that Nilakantan, in spite of many trials, has failed to find (220) extra reflections. This is quite at variance with the observations of Lonsdale and Smith (1941 c: cf. plate 8 (*a*) (*b*)), who have found 220 extra reflections of appreciable intensity in many different orientations. Lonsdale and Smith (1942 b) have also tested Pisharoty's other predictions from the Raman theory, namely, that the "forbidden" 222 reflection is an extra and not a Bragg reflection, and that there should be a 200 extra reflection of nearly the same intensity, and have found both to be quite incorrect. There is no 200 reflection of intensity even as much as 1 per cent of the observed 222 reflection, and the 222 reflection has all the characteristics of a normal Bragg reflection and none of those of an extra reflection (plate 8 (*c*)–(*f*)).

One word of caution may be interpolated here. In looking for possible reflections in "forbidden" positions, or at the edge of the Brillouin zone, it is essential that great care should be taken to ascertain whether any supposed effect is really due to the characteristic wave-length from the tube, or whether it may not be due to a sub-multiple of that wave-length. As mentioned before, even the most carefully monochromatized radiation contains unwanted components, which can quite easily amount to 1 per cent or more of the incident intensity. Lonsdale and Smith did indeed find a reflection in the 200 position (<1 per cent of the 222 intensity), but it was certainly due, mainly if not entirely, to a reflection by (400) planes of unwanted $\lambda/2$ radiation, of which the proportion present in the incident beam would only need to be 0·03 per cent in order to account for it completely.

§7. CRUCIAL EXPERIMENTS AND LIMITATIONS OF THEORY

Observations of the extra reflections from single crystals of metals have been most useful in deciding between the theories put forward. The breakdown of the simple diffraction theory in respect of these crystals has been indicated on p. 326. The Raman theory cannot explain the extra reflections from metals at all, except on the artificial assumption of infra-red characteristic vibrations of large amplitude unpredicted by normal lattice theory, and of phase-waves whose direction is unknown except in terms of the elastic forces whose importance the theory denies. The Faxén-Waller theory, as developed by Born, Sarginson and Jahn, explains the detail of the extra reflections from such metals as have been examined very simply and convincingly on the basis of the relative values and anisotropies of the elastic constants. In fact the only criticism that can be made is that the experimental and theoretical agreement found is almost too good. For the thermal theory is still only in the first stage of development, and assumptions are made in it whose validity is not altogether certain over the whole range in which it has apparently given satisfactory agreement with experiment. It is assumed that the amplitudes of vibration are small relative to the crystal spacings and that the effect of displacements of neighbouring atoms can be neglected. Let us briefly examine this point.

The mean K.E. of a vibrating atom (treated as a Planck oscillator) is given by

$$\tfrac{1}{2}m\overline{\xi^2}(2\pi\nu)^2 = h\nu\left(\frac{1}{2}+\frac{1}{e^{\beta}-1}\right).$$

Hence
$$\overline{\xi^2} = \frac{h}{2\pi m(2\pi\nu)} \cdot \frac{e^\beta + 1}{e^\beta - 1},$$

where β is $h\nu/kT$, m the actual mass of the atom, $\overline{\xi^2}$ the mean-square amplitude, $2\pi\nu$ the angular frequency, T absolute temperature and h and k the Planck and Boltzmann constants.

Assuming the vibration to be resolvable along three principal directions, the $\overline{\xi_x^2}$ normal to a single plane will be

$$\overline{\xi_x^2} = \frac{h}{6\pi m(2\pi\nu)} \cdot \frac{e^\beta + 1}{e^\beta - 1},$$

and this may be taken as the mean-square amplitude corresponding to a single transverse or longitudinal vibration. The limits of $2\pi\nu$ for the normal modes of vibration, and the values of $2\pi\nu$ corresponding to their maxima in the frequency spectrum of NaCl, are given by Kellermann (1940, 1941) as follows:—

(1) transverse acoustical: $0 \rightarrow 3{\cdot}0 \,.\, 10^{13}$ sec.$^{-1}$ (max. $N(\nu)$ at $1{\cdot}9 \,.\, 10^{13}$ sec.$^{-1}$);

(2) longitudinal acoustical: $0 \rightarrow 3{\cdot}5 \,.\, 10^{13}$ sec.$^{-1}$ (max. $N(\nu)$ at $3{\cdot}0 \,.\, 10^{13}$ sec.$^{-1}$);

(3) transverse optical: $2{\cdot}3 \,.\, 10^{13} \rightarrow 3{\cdot}6 \,.\, 10^{13}$ sec.$^{-1}$ (max. $N(\nu)$ at $2{\cdot}85 \,.\, 10^{13}$ sec.$^{-1}$);

(4) longitudinal optical: $3{\cdot}4 \,.\, 10^{13} \rightarrow 6{\cdot}0 \,.\, 10^{13}$ sec.$^{-1}$ (max. $N(\nu)$ at $4{\cdot}1 \,.\, 10^{13}$ sec.$^{-1}$).

Taking for m a mean atomic mass, the corresponding values of $\sqrt{\overline{\xi_x^2}}$ for a Na or Cl ion (considered as equivalent) will be, at 290° K.:—

(1) transverse acoustical: $\infty \rightarrow 0{\cdot}080$ A. (for max. $N(\nu)$, 0·125 A.);

(2) longitudinal acoustical: $\infty \rightarrow 0{\cdot}069$ A. (for max. $N(\nu)$, 0·080 A.);

(3) transverse optical: $0{\cdot}103 \rightarrow 0{\cdot}067$ A. (for max. $N(\nu)$, 0·084 A.);

(4) longitudinal optical: $0{\cdot}071 \rightarrow 0{\cdot}043$ A. (for max. $N(\nu)$, 0·060 A.).

The larger values of the acoustical amplitudes and the smaller values of the optical amplitudes will correspond to points near to the Bragg points in reciprocal space, the smaller values of the acoustical amplitudes and the larger values of the optical amplitudes to points half-way between these Bragg points. It will be seen that even the *minimum* values of $\sqrt{\overline{\xi_x^2}}$ are not negligible compared with the nearest distance between neighbouring atoms (2·814 A. from Na to Cl).

The very important x-ray measurements of James, Firth and Waller (1928) confirm the above calculations. They found 0·140 A. and 0·125 A. for the *average* values of $\sqrt{\overline{\xi_x^2}}$ for Na and Cl respectively in the NaCl crystal at room temperatures, giving a mean value which is very near to the "transverse acoustical" maximum $N(\nu)$ peak amplitude. If the average $\sqrt{\overline{\xi_x^2}}$ is as large as 0·13 A., it is fairly clear that much larger amplitudes must exist.

From Jahn's (1942) formulae it is also clear that for elastically anisotropic crystals the acoustical frequencies are lower, and, therefore, the values of $\sqrt{\overline{\xi_x^2}}$ are larger for waves travelling in some directions than in others. Calculations

based on known elastic constants (assuming wave velocity to be independent of wave-length) indicate that for transverse vibrations travelling along certain main crystallographic planes or axes, the amplitudes may be very much larger than the measured or calculated average, even for waves of short length. This is confirmed by the presence of non-radial extra streaks on photographs of KCl, benzil, Na, etc. (plates 1 and 6), which signify the existence of vibrations of very large amplitude travelling in the directions given by the streaks, the vibration wave-lengths having all values from infinity down to a length comparable with the unit-cell size. If these large vibration amplitudes were of the optical modes, neighbouring atoms or molecules moving in *opposite* directions, enormous crystal forces would be brought into action to resist the changes in inter-atomic distance thus caused. Short-wave acoustical vibrations of large amplitude could occur with far less strain on the crystal lattice, the *relative* movements of neighbouring atoms being small. The Faxén-Waller theory as it stands is not intended to apply in the short-wave regions, but since many of the most interesting experimental observations are made in that region, and since it does seem to be capable of application there, an extension of the theory is obviously desirable.

In view of the existence of these large amplitudes of vibration, even at room temperatures, and still more at high temperatures, it is not surprising that atoms occasionally break loose, as it were, and either interchange places with other atoms in the lattice or wander from one vacated place to another until they can reach a fault or a channel through which they can move still more easily. From this point of view, the problem of self-diffusion in metals or of electrical conductivity (forced diffusion) in ionic crystals is intimately related to the general dynamics of the lattice.

§8. CONCLUSION

It will be realized from the necessarily condensed account given above that this is a subject which is capable of expansion in many directions.

The observations already made form a direct experimental confirmation of the theory of lattice dynamics, and further study of the extra reflections for substances of simple structure should lead to better knowledge of the quasi-elastic forces between the atoms and molecules in the solid state, and of the changes in those forces with change of temperature.

A secondary method of crystal-structure determination is now available, to supplement the direct methods of Patterson-Harker and Fourier analysis. Conversely, it may be possible, using crystals of known structure, to study the atomic vibrations, particularly those of layer and chain structures, which present features of especial interest.

At present the need on the experimental side is for more accurate and comprehensive intensity measurements, and on the theoretical side for a more precise and detailed investigation of the x-ray diffraction at positions in reciprocal space not near to the lattice points, for large angles of deviation and at high temperatures, with proper allowance for the far from negligible amplitudes of vibration of each atom and of its neighbours.

§ 9. ACKNOWLEDGEMENTS

In preparation for this lecture I have received much inspiration from discussions with Sir William Bragg and Professor Max Born. I have also been privileged to consult Dr. Jahn's manuscripts before publication, and am grateful to him for this opportunity. My colleague, Mr. H. Smith, has spared neither time nor trouble in helping me to prepare suitable photographs for purposes of illustration.

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DISCUSSION

Sir WILLIAM BRAGG. Mrs. Lonsdale will describe the work which she has been carrying on at the Royal Institution for some time past. It deals with a phenomenon which may have been observed in the early days of x-ray crystal analysis, but has not been thoroughly investigated until recently ; Mrs. Lonsdale's study of it is by far the most complete up to date. These newly examined patterns present a novel method of examining the internal structure of solids. There is a wide field for investigation, and it is likely that important discoveries will be made in it. I should like to add that I have watched Mrs. Lonsdale's work with great interest, and have admired the skill and the untiring perseverance which she has spent upon it.

Dr. W. A. WOOSTER. I should like to ask whether effects resembling those described in the lecture, and attributed to elastic waves associated with the thermal motion of the atoms of the crystal, cannot be obtained by sending supersonic waves through the crystal. Some years ago x rays were reflected from vibrating crystals of quartz and a modification of the reflection was found. Has an explanation of these results been put forward on the basis of the present theory ?

A second point concerns a remark about the future development of this study. The lecturer stated that it might be possible to determine the elastic constants and their temperature coefficients by observations on diffuse spots. Would such observations depend upon a detailed investigation of the variation of density within a number of such spots ? If so, how can variations in the background round a spot due to the imperfect alignment of the constituent mosaic blocks be eliminated ?

Mr. G. D. PRESTON. In listening to Mrs. Lonsdale's lecture I have been impressed by the necessity of obtaining powerful sources of x rays, such as the 5 and 50 kw. tubes at the Royal Institution, for the study of these background reflexions by means of monochromatized beams. The attempt to explain the diffuse patterns by means of diffraction in a small group (the " simple diffraction hypothesis ") was made to avoid the mathematical complexities of the Faxén-Waller theory : it is not surprising that it fails to account for

all the details of the patterns, but it is interesting to find that it can predict some of the finer points of the Na patterns, as Sir William Bragg has recently shown (*Nature, Lond.*, **148**, 780 (1941)). Can the question, raised by Sir Lawrence, as to the reason for the accumulation of intensity near the normal reflexions, be answered in this way? The shortest compressional waves of length $2a$ require neighbouring atoms to move towards or away from one another, and it is unlikely that such a motion can have a large amplitude. A longer wave represented by a point close to a normal reflexion could have a proportionately greater amplitude without involving a greater relative displacement of neighbouring atoms. The success of the simple diffraction hypothesis may, I think, be partly due to the fact that it takes into account the relative immobility of neighbouring atoms by postulating a more or less rigid group of atoms. But the idea is evidently much too simple to afford a satisfactory explanation of the diffuse spots.

Arising out of Dr. Wooster's question, I think any imperfection in the crystal will produce background reflexions. Even if the imperfection is not a spatially periodic one, like the elastic temperature waves, it can be resolved into a Fourier series, each component of which will produce an effect between the normal spectra. Great care would be necessary in selecting perfect crystals for measurement of elasticity in the way suggested by Dr. Wooster.

Dr. G. T. Bennett. The calculation may be simplified as follows: From *Proc. Roy. Soc.* A, **179**, 334, the equation for r^2 is the expanded equivalent of

$$\begin{vmatrix} A_{11} & A_{12} & A_{13} & L \\ A_{21} & A_{22} & A_{23} & M \\ A_{31} & A_{32} & A_{33} & N \\ L & M & N & r^2 \end{vmatrix} = 0 \qquad \ldots\ldots(1)$$

or of

$$\begin{vmatrix} \beta+\delta l^2 & \gamma lm & \gamma nl & L \\ \gamma lm & \beta+\delta m^2 & \gamma mn & M \\ \gamma nl & \gamma mn & \beta+\delta n^2 & N \\ L & M & N & r^2 \end{vmatrix} = 0, \qquad \ldots\ldots(2)$$

where $\alpha=c_{11}$, $\beta=c_{44}$, $\gamma=c_{12}+c_{44}$, $\delta=\alpha-\beta=c_{11}-c_{44}$,

or of

$$\begin{vmatrix} \beta/l^2+\epsilon+\gamma & \gamma & \gamma & L/l \\ \gamma & \beta/m^2+\epsilon+\gamma & \gamma & M/m \\ \gamma & \gamma & \beta/n^2+\epsilon+\gamma & N/n \\ L/l & M/m & N/n & r^2 \end{vmatrix} = 0, \qquad \ldots\ldots(3)$$

where $\epsilon=\delta-\gamma$.

If

$$\left.\begin{aligned} \lambda &= \beta/l^2+\epsilon, \\ \mu &= \beta/m^2+\epsilon, \\ \nu &= \beta/n^2+\epsilon, \end{aligned}\right\} \qquad \ldots\ldots(4)$$

the determinant (3) is the eliminant of

$$\left.\begin{aligned} (\lambda+\gamma)x+\gamma y+\gamma z &= L/l, \\ \gamma x+(\mu+\gamma)y+\gamma z &= M/m, \\ \gamma x+\gamma y+(\nu+\gamma)z &= N/n, \end{aligned}\right\} \qquad \ldots\ldots(5)$$

$$r^2=(L/l)x+(M/m)\,y+(N/n)\,z. \qquad \ldots\ldots(6)$$

If $s=x+y+z$, equations (5) become

$$\left.\begin{aligned}\lambda x+\gamma s&=L/l,\\ \mu y+\gamma s&=M/m,\\ \nu z+\gamma s&=N/n,\end{aligned}\right\} \quad \ldots\ldots(7)$$

whence

$$\left.\begin{aligned}x&=\frac{L/l-\gamma s}{\lambda},\\ y&=\frac{M/m-\gamma s}{\mu},\\ z&=\frac{N/n-\gamma s}{\nu},\end{aligned}\right\} \quad \ldots\ldots(8)$$

and by addition

$$s=\Sigma\frac{L/l}{\lambda}-\gamma s\,\Sigma\frac{1}{\lambda}, \text{ giving } s, \quad \ldots\ldots(9)$$

and hence, also, x, y, z from (8) and r^2 from (6).

Dr. H. Wilman. The phenomena of the diffraction of fast electrons ($\sim$60 kv.) closely parallel those of x-ray diffraction except that there is often greater prominence of secondary and inelastic scattering effects, though it has been realized recently that secondary scattering is also noticeable throughout the whole field of x rays. This parallelism leads to the expectation that diffractions of the type which Mrs. Lonsdale has discussed and illustrated so elegantly should also occur in electron diffraction.

Such diffraction maxima, close to normal spots and comparable in size with them, have so far not been observed clearly in electron diffraction, although some of the patterns from anthracene (Charlesby, A., Finch, G. I. and Wilman, H., 1939, *Proc. Phys. Soc.* **33**, 479) show abnormal maxima which may be related to this kind of extra x-ray diffraction.* On the other hand, a much more diffuse set of prominent diffraction maxima accompanies the normal single-crystal spot pattern in many cases, notably those of molecular crystals. In 1935 I obtained some photographs (see Finch, G. I., Quarrell, A. G. and Wilman, H., 1935, *Trans. Faraday Soc.* **31**, 1050, fig. 32) from thin anthracene crystals, showing spots strengthened in regularly-spaced regions whose spacing and arrangement appeared to correspond to the linked benzene-ring structure of the molecules. Further photographs (Finch, G. I. and Wilman, H., 1937, *Ergebn. exakt. Naturw.* **16**, 353) showed, beside the spot pattern, strong diffuse maxima in regular rows or in parallel bands ; and diffuse bands in transmission patterns were also yielded by long-chain hydrocarbons and their derivatives. A detailed study of anthracene was made in 1939 (Charlesby, A., Finch, G. I. and Wilman, H., *loc. cit.*), and this showed that the diffuse maxima corresponded very closely in position and shape, and qualitatively in relative intensities, with those to be expected from molecules occupying the same orientations as those in the crystal, but diffracting the electron beam independently. From a comparison with the theoretical scattering distribution, it was concluded that the diffuse maxima were best explained as due to thermal vibrations of the practically rigid molecules about their mean positions in the crystal.

While this work was being prepared for publication we learned that Mr. Preston was writing an account (Preston, G. D., 1939, *Proc. Roy. Soc.* A, **172**, 116) of his x-ray work which first showed clearly the temperature dependence of the intensity of the x-ray extra diffractions from non-molecular crystals. The two sets of results appeared to be related, in that the small coherently vibrating atom groups postulated by Preston were analogous to rigid molecules, and Sir William Bragg's more general demonstration (Bragg, W. H., 1941, *Proc. Roy. Soc.* A, **179**, 51, 94), that the positions of the x-ray extra maxima correspond to diffraction from small crystal units consisting of an atom and its nearest neighbours, brings out the analogy very clearly.

Hitherto no maxima of the very diffuse electron-diffraction kind have been obtained

* A closer investigation of these abnormal diffractions, and comparison with the x-ray results now available, has shown that they are in fact identical in nature (see Charlesby, A. and Wilman, H., 1942, *Nature, Lond.*, **149**, 411).

H. WILMAN (Discussion on *X-ray study of crystal dynamics*, by K. LONSDALE).

The two figures below were inadvertently omitted from the discussion on the above paper (this vol., part 4, page 350).

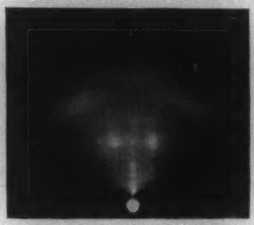

Figure 1. 5.6-cyclo-penteno—1.2-benzanthracene crystallized in one-degree orientation on polished stainless steel.

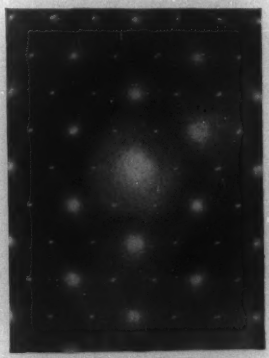

Figure 2. Cadmium iodide, beam along [001], showing diffuse lines along the main spot rows.

To face page 350

in x-ray patterns from molecular crystals in addition to the other extra spots. It appears that the very diffuse maxima, even if present, would mostly fall outside the field of diffraction recorded in x-ray Laue patterns, and their presence or absence is thus not yet demonstrated.

That the diffuse electron maxima are not due to a surface effect seems to be shown by the fact that the molecules giving rise to them are oriented just as in the crystal interior, and further, reflection patterns (figure 1) from the smooth flake-like crystals in (one-degree oriented) films grown from solution are essentially similar to the transmission patterns. The mode of dependence of the intensity of these maxima on crystal thickness has not yet been clearly demonstrated. Although the theory (Charlesby, A., Finch, G. I. and Wilman, H., *loc. cit.* 1939) indicated that the ratio of the maximum intensity in a diffuse maximum relative to the intensity maximum in a Bragg spot should decrease with increasing crystal thickness, it seems that the effect of the usually appreciable beam divergence in the case of x-ray diffraction will tend to reduce or annul this decrease, since the intensity maximum in a Bragg spot will then be proportional to the number of atoms in the thickness of the crystal sheet, instead of proportional to its square. Under these conditions the diffuse type of maxima may well also occur in the x-ray patterns for which thicker crystals are used.

Diffuse lines along principal spot rows in electron-diffraction transmission patterns are yielded by some crystals, for example phthalimide (Finch, G. I. and Wilman, H., 1937, *loc. cit.*), anthracene, stearic acid, dodecylalcohol, graphite, molybdenite and cadmium iodide (figure 2). These are probably similar in nature to the lines described by Mrs. Lonsdale, and presumably originate from the strong anisotropy of the crystal relative to elastic waves passing through it. Similar diffuse lines have been observed in some silver patterns (Goche, O. and Wilman, H., 1939, *Proc. Phys. Soc.* **51**, 625), but these may be due to a remnant of the initial twinned structure of the silver layer, not completely removed by heat treatment.

To conclude, it seems to me that any theory of diffraction by crystals undergoing thermal vibrations should be capable of explaining the electron-diffraction phenomena as well as those of x rays ; and I should be very interested to know whether the Faxén-Waller theory can account for the diffuse electron maxima, and whether a more conclusive search for similar x-ray maxima could be made.

Dr. W. H. Taylor. I wish to ask Mrs. Lonsdale for information about the use of the new technique in the examination of crystal structures. She has used experimental data obtained from crystals of known structure in order to elucidate the nature and origin of the " extra reflections ". To what extent has this process been inverted in seeking information as to the structure of a crystal not previously examined by standard methods ?

Mr. F. A. Bannister. It follows from the work of Laval, Mrs. Lonsdale and Jahn that substances with the same crystal structure, but possessing quite different elastic constants, show marked differences in the distribution of diffuse spots. What does this imply for the two types of diamond photographs recently published by the lecturer ?

The variation in the size of the diffuse spots with temperature might yield a decision between the Faxén-Waller and Bragg theories.

Author's reply. Effects resembling those described in the lecture ought, of course, to result from any forced crystal vibrations, but in the case of ultrasonic waves of large amplitude, the wave-lengths will be so large that the ends of the corresponding wave-vectors will lie in the very close neighbourhood of the reciprocal-lattice points, and any extra reflection that occurs will probably result only in a redistribution of intensity within the Bragg spots. Increases in the absolute intensity of the Laue reflections have been reported (Fox and Carr, 1931 ; Nishikawa *et al.*, 1934 ; Klauer, 1935) for quartz crystals vibrating piezoelectrically, but this has been explained as due to a decrease in primary or secondary extinction (Jauncey and Bruce, 1938 ; Fox and Stebbins, 1939). The inference is that the existence of forced vibrations amounts to a change in the " mosaic condition " of the crystal. A change in intensity of the transmitted (central) beam during oscillation of quartz crystals has also been reported (Fox and Fraser, 1935) and denied (Jauncey *et al.*, 1935, 1936 ; Fox and Stebbins, 1939). The continued sharpness of the

transmitted beam is to be expected from the Faxén-Waller theory (Weigle and Smith, 1942).

The second point raised by Dr. Wooster is one of considerable interest. I am not convinced at present that *in general* the existence of a mosaic condition, apart from that imposed by the heat vibrations themselves, is proved. The volume of the Faxén-Waller " temporary super-lattices " corresponding to the maxima of the frequency-distribution curve of (say) NaCl is about (10 A.)^3, but there exist also super-lattices of all sizes up to that of the crystal itself. Although these are temporary, they will have the same effect in reducing extinction as would a static breaking up of the crystal. If we suppose, however (as is certainly sometimes the case), that a static mosaic exists, I think that a study of the crystal at different temperatures would distinguish the one effect from the other. Examination of a single photograph would not be sufficient. A detailed investigation of the density variation within all observable extra spots and streaks will give the distribution of extra scattering power in reciprocal space within the limiting sphere, and in particular the distribution about different reciprocal-lattice points of both lower and higher orders. If the mosaic blocks are sufficiently small (say $<$(50 A.)^3) and disoriented (say by several minutes of arc or more) to produce background effects at all, then such extra reflections will be of the kind predicted by the simple diffraction theory, and will be temperature-insensitive. They will also have larger areas at large angles of total deflection. As a rule, however, the constituent blocks of a static " mosaic crystal " are not small enough, nor are they disoriented enough, for background effects to be expected. A most useful diagram showing the influence of crystal imperfection on the integrated intensity of x-ray reflection has been given by Ewald and Renninger (1935). The conditions implied by the question would only exist in the limiting case represented by the lower right-hand corner of the diagram.

I cannot agree with Mr. Preston that care would have to be taken to choose perfect crystals for investigation. Such crystals are not available, and the Faxén-Waller theory, as it stands, does not apply to perfect, but to ideally imperfect, crystals. As far as I know, the effect of thermal vibrations on a perfect crystal has not yet been theoretically considered ; no doubt the introduction of such statistical imperfections would profoundly modify the " perfect crystal " reflection formula. An attempt has already been made by Hall (1942) to estimate the elastic constants of KBr by means of observations of extra reflections, using Cu Kα radiation. Chemical purity and the absence of surface or other gross forms of distortion would be essential requirements for accurate and reproducible measurements.

When Mr. Smith and I first obtained extra-reflection photographs from crystals of organic compounds, the possibility that our diffuse maxima (especially in the case of benzil) might be similar to those observed for anthracene by Charlesby, Finch and Wilman was very much in our minds. As Drs. Charlesby and Wilman have pointed out, however, maxima of the electron-diffraction type would only be observable using very short x-ray wave-lengths, molecules of high internal periodicity and large-angle deflections. Even then they would be so diffuse as to cover very large areas of the background, and it is doubtful whether any really satisfactory observations could be made. It must be remembered that the reciprocal-lattice area covered by a single electron-diffraction photograph is many times larger than that explored by means of an x-ray photograph. I believe that the conditions of the different experiments also imply a further distinction between the methods. The use of a very thin film in the electron-diffraction method involves the extension of all reciprocal-lattice points along one direction in reciprocal space and the absence of long thermal waves in that particular direction. In effect the electron-diffraction method examines only two-dimensional thermal vibrations, the x-ray method three-dimensional ones. The two methods could perhaps best be made to overlap by a study of films of long-chain compounds or of substances of very high molecular weight and internal regularity. The Faxén-Waller theory could probably be extended to account for the diffuse electron maxima, but at present it does not include them.

The use of " extra " reflections in the examination of crystals of unknown structure has so far only been applied to fairly complicated organic compounds in which there is a chance that a layer or chain (or combined layer and chain, i.e. a lath-like) arrangement of molecules might occur. Either of these arrangements is most readily identified from a few

well-exposed Laue photographs ; and the position of the layer or chain relative to the crystal axes can be unequivocally located. The method is not, of course, a substitute for the standard methods of analysis, but it has already given most useful supplementary, and even " leading ", information (Lonsdale, 1941; Lonsdale, Robertson and Woodward, 1941 ; Knaggs and Lonsdale, 1942).

The differences in the extra reflections from the two types of diamond cannot be explained as due to differences in the elastic constants, but, as Mr. Preston has remarked, any crystal imperfection, even if not spatially periodic, will produce a background effect, which may or may not be observable. The strength of the structure-sensitive secondary extra reflections from normal (type I) diamonds (and their temperature-insensitiveness) indicates a spatially periodic imperfection which in some specimens may attain considerable magnitudes.

No exact measurements of the size and intensity of the extra reflections over a range of intensity has yet been made for any substance for comparison with the predictions of the Faxén-Waller theory. An estimate of the expected effect according to the Bragg theory would be very difficult to make ; but if it is assumed that the effect of increasing temperature would be the breaking up of the structure into more and smaller crystallites, then, from a very general point of view, both theories would lead to the same expected result, an increase in both size and intensity of the extra reflections, particularly in those far from reciprocal-lattice points and of high order. I do not think that this could be made a crucial experiment, although the reversible changes with temperature which are experimentally found prove, of course, that no *temperature-independent* breaking up of the crystal into small groups can possibly explain the observed phenomena.

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THE SECONDARY X-RAY SPECTRUM OF SYLVINE: THEORY AND EXPERIMENT

By (the late) Sir WILLIAM BRAGG, O.M., K.B.E., F.R.S.

MS. received 31 *May* 1942

Note by Sir Lawrence Bragg, F.R.S. and Mrs. Kathleen Lonsdale

This paper was written by the late Sir William Bragg shortly before his death, and was left in such a form that publication is possible, though we have ventured to make certain small alterations or additions where the original was incomplete, and have provided an abstract. The treatment of the extra reflections which appear at high temperatures is generally by means of the reciprocal lattice. Sir William Bragg expressed his results without making use of this analytical device, but in order to examine the correspondence between reciprocal and direct treatments he wrote a special section which appears in the paper. In the reciprocal treatment, the diffuse extra reflections, whose strength is enhanced by rise of temperature, can be represented as a cloud surrounding each point of the reciprocal lattice. This feature, equivalent to the construction in figure 1, follows equally either from the hypothesis that the spots are due to modulations of the lattice by thermal waves, or from the hypothesis that there are in the crystal small regions which are out of phase with each other in a completely random way. The main point made in the present paper is that the latter hypothesis, which leads to a simple optical treatment of the diffraction, is in better accord with the form of the observed spots in the case of KCl.

ABSTRACT. The co-existence in a crystal of very large and very small groups of atoms, the atoms within any group being in correct relative positions, but out of alignment with the atoms of neighbouring groups, so that all phase relationships between the scattered x-ray waves from successive groups is lost, would give both sharp Laue spots and diffuse background spots on a Laue photograph. This hypothesis predicts nearly circular diffuse spots for KCl at small angles of total deflection, whereas the Faxén-Waller theory, using known values of the elastic constants, predicts diffuse spots in the shape of elongated ellipsoids of maximum intensity at the centre. It is claimed that in this respect the hypothesis that the crystal is broken up into groups of atoms, with loss of continuity in phase relationship, is in better accord with observation than the hypothesis that it remains a single crystal distorted by the heat waves, but with no loss of continuity.

The *extra pattern* in the diffraction of x rays by crystals has lately been explained as due to interaction between waves of the x rays and the thermal waves within the crystal. The theory on which the explanation is based has been discussed by Faxén, Waller, Laue, Ott, Zachariasen, Born and Sarginson, and Jahn. On account of the relations between the thermal movements and the elastic constants of the crystal, the calculated results can be expressed in terms of these elastic constants when they are known, and may then be compared with the experimental results.

In 1938 G. D. Preston made one of the first experimental examinations of the extra pattern. His crystals were NaCl, Al and MgO (Preston, 1939). He ascribes the effect, not directly to thermal movements, but to the presence of very small groups of atoms, each group a crystal in itself, imperfectly aligned with the main body of the crystal and therefore acting incoherently.* As will be shown presently—although this is not generally recognized—the hypothesis explains the extra pattern at least as well as the previous theory. It has, however, been objected to on various grounds, the principal being, in the first place, that it is unnecessary since the elastic-constant theory is sufficient, and, in the second place, that the presence of these small groups and their supposed mode of action would be difficult to reconcile with other crystal effects.

Nevertheless, it seems worth while to examine this theory, even if its fundamental assumptions are not warranted. It is remarkable that two theories which seem to be entirely different should lead to results which are very much alike, and are in more or less agreement with all experiments so far made. It may well be that though the two theories are formally different, they are actually linked closely together.

Let us then provisionally assume Preston's theory, and compare its predictions with experiments.

A very small group of atoms scatters an incident beam of x rays in a more diffuse manner than a crystal of larger size. In fact the diffuseness is often used as an indication of the size of the group.

Most of the experiments which lend themselves to the comparison between these theories and experiment have been made with crystals which are actually monatomic, such as diamond and sodium, or effectively so, such as sylvine. The crystal structure of the latter is formed by the repetition of the atom at constant intervals in three directions, so related that three single displacements, one in each direction, form three edges of a unit cell: that is to say, a parallelopiped having atoms at its corners only, and none within it or on its faces.

Suppose that a group is a larger parallelopiped whose edges are parallel to the three chosen directions, and that there are p atoms on one edge, inclusive of those at each end, q on another, and r on the third; then the amplitude of the scattered ray is proportional to

$$\frac{\sin p\phi_a/2}{\sin \phi_a/2} \cdot \frac{\sin q\phi_b/2}{\sin \phi_b/2} \cdot \frac{\sin r\phi_c/2}{\sin \phi_c/2},$$

where ϕ_a, ϕ_b, ϕ_c are the differences in phase between the rays scattered at that

* *Preston, p.* 122, *loc. cit.* "The fact that the intensity of the spots increases as the temperature of the crystal is raised suggests that their presence is connected with the temperature vibrations of the lattice . . . The effect of this wave-like disturbance of the regularity of the lattice is to produce a series of "ghosts" associated with the normal spectra; if the disturbance consists of a very large number of lattice waves these will produce a continuous faint background on the Laue photographs. The experiments described above show that this background is not of uniform intensity but possesses well-marked maxima. The simplest explanation of the presence of these maxima (in aluminium single crystals) is to suppose that the thermal vibrations are of such a nature that the crystal is divided up into small groups of atoms; in each group the face-centred arrangement is accurately maintained, but neighbouring groups have slightly different spacings due to a wave of dilation, or are inclined at a small angle to the average direction of the crystal as a result of a wave of shear." [*Note added by Sir W. L. Bragg and Mrs. K. Lonsdale.*]

corner of the cell which has been chosen as origin and the three neighbouring corners respectively.

If the direction cosines of the scattered and incident rays, referred to rectangular axes having the chosen corner as origin, be h, k, l, h', k', l' respectively, if x_1, y_1, z_1 be the coordinates of the atom at the end of the first repetition along the first axis, and so on, and if λ be the wave-length, then

$$\phi_a = \frac{2\pi}{\lambda}\{(h-h')x_1+(k-k')y_1+(l-l')z_1\}.$$

In the case of a group consisting of a single cell, there are two atoms on each edge, and the expression reduces to

$$8\cos\phi_a/2 \,.\, \cos\phi_b/2 \,.\, \cos\phi_c/2.$$

Whatever the value of p, q, r, the expression is at a maximum when ϕ_a, ϕ_b, ϕ_c are all multiples of 2π. In this case, the corners of the unit cell, and the atoms throughout the group, are in phase with each other, as in the case of a Bragg reflection. There are subsidiary maxima when only two of the three differences of phase are multiples of 2π: and others of still less importance when only one of them is such a multiple.

In any given case when the relative coordinates of the cell corners and also the direction of the incident ray are known, equations may be formed which are the condition for the realization of the maxima. In practice it is convenient to let the incident rays be parallel to one axis: thus its direction cosines may be taken to be 001. Then the maxima occur when

$$\begin{aligned} hx_1+ky_1+(l-1)z_1 &= M_1\lambda, \\ hx_2+ky_2+(l-1)z_2 &= M_2\lambda, \\ hx_3+ky_3+(l-1)z_3 &= M_3\lambda, \end{aligned}$$

where M_1, M_2, M_3 are any integers, λ is the wave-length, and x_1, y_1, z_1; x_2, y_2, z_2; x_3, y_3, z_3 are the coordinates of the three corners of the cell nearest to the origin. These equations give the values of h, k, l for which the corner of the cell chosen as origin are in phase with the three neighbouring corners respectively. They may be looked on as the equations in h, k, l of planes cutting the sphere $h^2+k^2+l^2=1$.

Choosing any two of the three direction cosines, such as h, k, curves may be plotted which represent the projection of the intersections of planes and sphere upon a plane perpendicular to the incident ray. In practice, this plane generally coincides with that of the photographic film or plate, so that there is a direct and simple relation between h, k and the position of the point on the plate where the scattered ray strikes it. If ξ, η are the coordinates of that point referred to axes parallel to the main axes, but having as origin the point where the direction of the incident ray strikes the plate, then $\xi = hD/l$, $\eta = kD/l$, where D is the distance from the crystal to the plate.

The adjoining figure 1, which is reproduced from an article in the *Proceedings of the Royal Society* (W. H. Bragg, 1941), illustrates these points. The crystal is sylvine, which may be considered to be a simple cubic crystal of side 3·14 A. The incident Mo rays, for which $\lambda = 0{\cdot}71$ A., make an angle of 20° with one face of the cube and are parallel to an adjoining face. The coordinates of the three

corners referred to the fourth, as described above, are then $(a\cos\theta, 0, -a\sin\theta)$: $(0, a, 0)$: $(a\sin\theta, 0, a\cos\theta)$, where $a=3{\cdot}14$, $\theta=20°$.

The equations become

$$a\{h\cos\theta-(l-1)\sin\theta\}=M_1\lambda,$$
$$ak\qquad\qquad\qquad=M_2\lambda,$$
$$a\{h\sin\theta+(l-1)\cos\theta\}=M_3\lambda.$$

When arithmetical values are given to the quantities a, θ and λ, three sets of (h, k) curves for integral values of M_1, M_2, M_3 can be calculated. The (ξ, η) curves are readily derived, by means of the relations given above, and are shown in the figure, the scale being chosen so that D, the distance from crystal to plate, has the value 10. The first equation gives the curves which are approximately vertical; the second, those which are approximately horizontal; and the third the three more widely spaced curves, of which one is almost a semicircle. Only one-half of the complete diagram is shown, the second half being the image of the first.

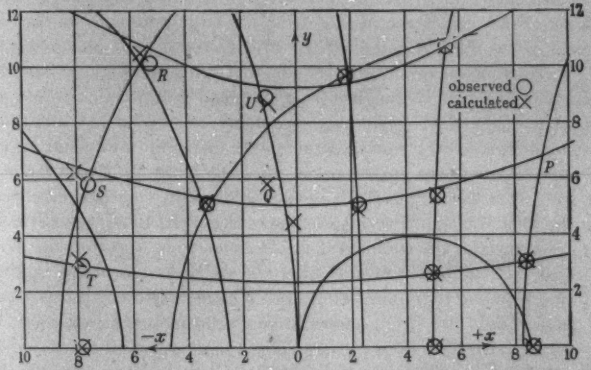

Figure 1.

Although there is in this diagram no triple point of intersection of members of the three sets of curves, there are several places where three curves nearly meet in a point. When that occurs, the corners of the unit cell are nearly in phase with each other and an observable scattering becomes a possibility. If members of the three sets met in a single point, there would be a Bragg reflection for the particular direction (h, k) given by the coordinates of that point. The small round circles show where the maxima of the extra spots under discussion are observed in the photograph; it will be observed that their positions coincide with expectation to a remarkable degree. Spots are found where members of the first two sets of curves intersect, provided a member of the third set is not too far away.

For the purpose of a closer comparison between theory and experiment, the positions of the maxima have been calculated for the case when $p=q=r=2$, i.e. the amplitude has been put proportional to $\cos\phi_a/2\,.\,\cos\phi_b/2\,.\,\cos\phi_c/2$. Whatever the actual values of p, q and r, the positions of the principal maxima

are not sensibly affected: groups of more than the eight atoms at the corners of a cubic cell have secondary maxima in various positions, and these add a diffused background which diminishes the contrast between the primary maxima and their surroundings. The calculated values are marked by crosses, and their close agreement with the small circles shows that the theory gives in this case a satisfactory explanation of what is observed. Theory presumes the existence of small groups of no particular shape in slight disarray with the main crystal and with one another. The slight disarray does not prevent them from acting simultaneously. If the crystal is so set that the main body is giving a Bragg reflection, the action of the groups will merely cause a little diffused effect on either side of the main reflection, which, moreover, will absorb most of the energy, and the diffused effect will consequently be weaker.

Suppose that there was a small group alongside a large one, ranged more or less parallel to it. If, then, a beam of monochromatic rays fell upon the two, and the inclination of the pair to the beam were gradually altered, over a range which covered the point where the incident rays experienced a Bragg reflection in the large crystal, then the reflection from the large group would flash out at the moment when the inclination of the rays to the crystal planes was right, but would vanish at all other angles. On the other hand, there would be a reflection—much feebler, of course—from the small group which would persist over a certain angle which might be considerable, say 10° or 20°. At the same time the inclination of the scattered ray to the incident would not vary very much, as generally happens in the case of diffraction gratings, and is found to be the case with these extra spots. The extra spot would not change its position much on the plate during the turning of the crystal; the Bragg reflection would flash out for an instant, and would at that instant coincide with the other spot.

If the radiation contained rays of other wave-lengths (including that of the strong monochromatic ray), there would be no change in the extra-spot phenomenon, because only the strong monochromatic beam could produce it. But there would be a reflection from the large group of atoms at all times; whatever the position of the crystal, the white radiation would include some wave-length which would be reflected by the large group. During the turning, the resulting spot would move towards the extra spot and go through it. The extra spot would brighten at the approach of the reflection from the large group, because when the inclination is right for reflection from the large group it is at least nearly right for reflection from the small group, the planes of the two being at least approximately parallel.

The form of the extra spot is nearly circular in most cases, certainly when the spot, as in the photograph corresponding to figure 1, is one of the dozen or so spots near the origin. Calculations based on the formulae already given agree with this experimental result: it is, in fact, to be expected from the simple causes of its origin as given by the theory at present under consideration. The small groups are supposed to consist of atoms few in number in each case; and in each case the atoms are arranged among themselves in the manner of the particular crystal to which they belong. They may be of any form provided that the average form is spherical, that is to say, there is no preponderance of the dimensions of the groups in particular directions.

In the foregoing, an immediate comparison is made between theory and experiment by putting together the sylvine photograph and the corresponding (h, k) diagram with its immediate derivative, the (ξ, η) diagram.

In 1938 and 1939 Laval described a long and careful series of measurements of the background x-ray diffraction, which is equivalent to saying that he investigated the extra-spot effect. He used an ionization spectrometer: keeping the spectrometer fixed, and, therefore, confining attention to a particular value of (h, k), he examined the result for different positions of the crystal. In the photographic method the crystal is fixed, and all values of h and k are considered simultaneously. It is not a simple matter to compare in detail the results obtained by the two methods, but the general result is quite clear. Laval's experiments agree, so far as can be seen, with those of the photograph, as must be the case because the subject is the same. Laval's results are expressed in terms of a reciprocal lattice, and it is convenient therefore to use this lattice in an examination of his results and a comparison of them with the (h, k) diagram. Expression of results in terms of the (h, k) diagram and expression in terms of the reciprocal lattice can be linked together in the following simple way.

Suppose that in figure 2, IC represents the direction of a bundle of monochromatic x rays incident on a crystal at C. Let this direction be the axis of z, and let the axis of x be in the plane of the paper, as shown, and the axis of y be perpendicular to that plane.

Let (h, k, l) be the direction cosines of any line CQ which does not necessarily lie in the plane of the paper.

Let RR′ and CP be the external and internal bisectors of the angle ICQ lying in the plane ICQ. Let (l', m, n) be the direction cosines of CP. Then $h = -2l'n$; $k = -2mn$; $l = 1 - 2n^2$ and $n = \sin \text{ICR}'$.

Let $\text{CP} = 2K^2n/\lambda$, where K is a constant for different values of h, k. The locus of P is a sphere with centre O and radius OC, as shown in the figure, because if PI′ is perpendicular to CP, then $\text{CI}' = \text{CP}/n = 2K^2/\lambda$ (O is the mid-point of CI′).

Let A be any point; let $\text{CA} = a$; and let (p, q, r) be the direction cosines of CA. If rays parallel to (001) are incident on C and A, and are scattered in both cases in the direction (h, k, l), the difference in length of path of the two rays is

$$pah + qak + ra(l-1),$$

since x, y, z for A will be pa, qa, ra.

If the scattered rays are in phase, this quantity is an integral multiple of λ. Then

$$\begin{aligned} M\lambda &= pah + qak + ra(l-1) = -2pal'n - 2qamn - 2ran^2 \\ &= -2na(pl' + qm + rn) = -2na\cos \text{PCA} \\ &= -\frac{\lambda a}{K^2} \cdot \text{CP} \cos \text{PCA} \quad \left(\text{since } 2n = \frac{\lambda}{K^2} \cdot \text{CP}\right) \\ &= -\frac{\lambda a}{K^2} \cdot \text{CA}', \text{ where CA}' \text{ is the projection of CP on CA.} \end{aligned}$$

Hence $\text{CA}' = M \cdot K^2/a$, where M is any integer.

If, therefore, the values of h, k are such that C and A are in phase, P lies

on a plane passing through A′ and perpendicular to CA: this is the reciprocal plane of the point A.

As a result of the definition, P must also lie on the sphere of radius K^2/λ, centre O, and has no significance unless it does so. This is really equivalent to the statement that the values of h, k, l are such that $h^2+k^2+l^2=1$.

If one corner of the cubic cell of sylvine be taken as origin, an adjacent corner is in phase for a given value of h, k if the point P corresponding to $(h\ k)$ lies on one of a set of parallel planes spaced at intervals of K^2/a, one of them $(M=0)$ going through the origin. In practice it is convenient to make the radius of the sphere K^2/λ equal to 10 units. The spacing is therefore $10\lambda/a$; when Mo rays are used, this is equal to 2·26.

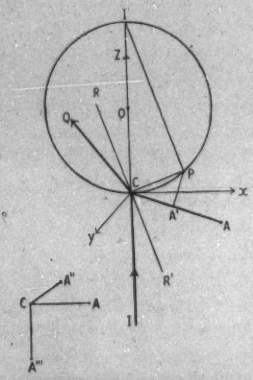

Figure 2. Q, RR′, P, A and A′ are not necessarily in the plane of the paper, although they have been drawn in that way for convenience.

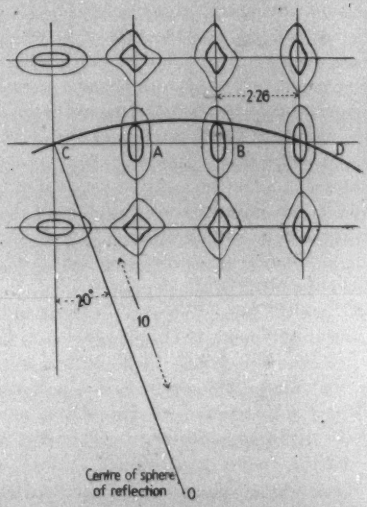

Figure 3. Isodiffusion surfaces and part of sphere of reflection for KCl. $\theta_{100}=20°$ MoKα radiation; as calculated from Faxén theory.

The triple series of planes corresponding to the three cube corners A, A″, A‴ forms a set of cubic boxes. If the point P lies on a circle of intersection of any of these planes by the sphere, the corresponding values of (h, k) are those for which the origin and one other of the cube corners are in phase. If it lies at a point where the sphere cuts a line of intersection of two planes, then for that value of (h, k) three corners of the unit cell are in phase with each other. If the relative orientations of the incident ray and the crystal happen to be such that the sphere passes through a triple point of intersection, then for the corresponding value of (h, k) there is a Bragg reflection of the monochromatic ray.

With each position of P may be associated a quantity proportional to the intensity of the ray scattered in the corresponding (h, k) direction, which can, of course, only have an existence when sphere and crystal are so adjusted that

the sphere passes through that position. At a triple point, which Laval calls a node, the intensity is a maximum and falls away if P moves away from that point in any direction. Laval has mapped out this field round a nodal point of sylvine and found it to be of a globular form, rather flattened on one side. This result may be compared with that of the photographic method in the following way:—

When P is projected upon the xy plane, its coordinates are l'. CP and m. CP, which are equal to $2K^2l'n/\lambda$ and $2K^2mn/\lambda$, or $-K^2h/\lambda$, $-K^2k/\lambda$.

When K^2/λ is put equal to 10, then these coordinates are equal to $-10h$ and $-10k$ respectively.

Thus the intensity associated with any position of P when projected on the xy plane is the same as that corresponding to the point (h, k) in the (h, k) diagram. As this latter is very nearly a true map of the intensities of the photograph, at least when l is nearly equal to 1, so also is the map formed by the projection of all the points P, where the sphere cuts the field round the node, the corresponding intensity defined by the field being associated with the projection at each point. A test of this construction shows that the spots are approximately circular when the spots are fairly close to the origin: and the intensity field round the node must be such that the projection is of circular form, with a maximum at the centre and an equal fading away in all directions. Laval's results satisfy the test fairly well.

This condition is, however, far from being satisfied if the field round a node is as calculated on the theory of Faxén and subsequently developed by several other writers. Mrs. Lonsdale has been so kind as to draw for me maps of sections of the reciprocal lattice, from which figure 3 is an extract. The plane of the section is perpendicular to the y axis and goes through C. The incident rays are in the plane of the paper, and are, as before, taken to define the axis of z; and one side of the squares is inclined at 20° to the axis of z. Calculation based on the Faxén theory indicates that the reflecting regions or " fields " round ABC are oblate solids of revolution, in which the small axis along the edge of the cube CABD is less than one-half of the longer axes in the other principal directions. The section of these solids of revolution by the sphere in the neighbourhood of A, B and D is in each case nearly of elliptical form.

The projection of the section upon a plane perpendicular to the axis of z gives the form of the corresponding spot in the photograph, which thus, according to the Faxén theory, should be elongated. On the other hand, the small-group hypothesis gives round spots, and this, it is claimed, corresponds more nearly to the form actually observed both by Laval's measurements and in photographs.

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LATTICE DYNAMICS AND X-RAY SCATTERING

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ABSTRACT. The " extra spots " on Laue photographs are considered by many investigators in Europe and America as due to the thermal motion of the crystal lattice, but a group of Indian physicists led by Raman have proposed a different theory which they claim to be based on the assumption of a new specific quantum effect. Raman criticizes in particular the current theory of lattice vibrations as it makes use of the *method of the cyclic lattice*, which he considers wrong. The present paper refutes these criticisms. It is shown that the cyclic solution is in complete agreement with the rigorous solution in the case of a diatomic linear lattice where an optical branch exists in addition to the acoustical one. Raman's theory is compared with the dynamical lattice theory, which can be developed on rigorous quantum methods, while Raman's considerations are essentially classical. His main error consists in considering the velocity of wave propagation in a lattice as constant ; in fact, it is a function of the wave number, which for the acoustical branches varies in such a way that the intensity of scattering has maxima in the neighbourhood of the Laue spots. Hence the extra spots are due to the acoustical branches, not the optical ones, as Raman contends. The paper further contains a short account of the results of the dynamical theory obtained by Zachariasen, Jahn, and Sarginson, which are in good agreement with the experiments of Lonsdale and Smith, Zachariasen and others.

§1. INTRODUCTION

THE theory of the new type of spots on Laue photographs (" extra spots ") is still in a controversial state. The thermal theory * (Debye, 1913 and 14; Faxén, 1923; Waller, 1923, 1928), which is accepted by Lonsdale and Smith (1941), Zachariasen (1940, 1941) and other investigators, is opposed by Sir C. V. Raman (1942), who claims that the extra spots are due to a peculiar new quantum effect. His ideas are described in detail in a special number of *Proc. Ind. Acad. of Science*, which is completely devoted to papers on the new phenomenon. In order to justify his assumptions, Raman rejects some well-established results of the general theory of lattice dynamics, namely, the statement that the elastic spectrum consists of a set of branches or bands, each containing N frequencies (where N is the number of cells), and that the density of the frequencies in each band is uniform in the space of wave numbers. Raman declares that this distribution applies only to the low-frequency (or acoustical) branch which is used for the calculation of the specific heat (Debye's formula), whereas instead of the high-frequency (optical) branches there are sharply monochromatic vibrations. He believes that he has strong experimental evidence for this view. I shall not enter into the question of the experimental confirmation of the different theories, as Mrs. Lonsdale, in her lecture, has done this much more expertly. I shall restrict myself to the discussion of the

* My own work, partly in collaboration with Miss K. Sarginson (the first part of which appeared last year), is a modernized and more rigorous form of Waller's theory.

theoretical side of the problem. Raman also puts forward theoretical arguments for his view; he considers as the weak spot of the lattice dynamics the assumption of the *cyclic lattice*. I quote his words: "The so-called postulate of the 'cyclic lattice' is in fact nothing more than an *ad hoc* hypothesis adopted for mathematical convenience", and he adds a critical examination of it, which culminates in the assertion that the usual method of Fourier analysis of the atomic vibrations "would result in the phases of the individual oscillators being entirely arbitrary and uncorrelated with each other. This is evidently *a reductio ad absurdum*, since such a state of affairs could only exist when the Planck oscillators are entirely independent of each other, as would be the case if we were considering the molecules of a gas. It is a fundamental aspect of the crystalline state that the oscillators of which it is composed are coupled to each other more or less firmly". The last remark seems to me due to a misunderstanding. In lattice dynamics the atoms are, of course, supposed to be coupled to each other. Just because they *are* coupled, they do not represent Planck oscillators to which quantization could be applied. But if the forces are linear in the displacements, one can always introduce normal coordinates which are independent oscillators and can be quantized. They are used in the statistical mechanics of crystals (specific heat, thermal expansion, etc.), and it is obvious that they also provide the method of treating the influence of lattice vibrations on x-ray scattering (Debye 1913–14).

More important is Raman's critical attitude to the method of the cyclic lattice; for it is perfectly correct that it was invented (Born, 1923) for mathematical convenience, and that there is no proof apart from an almost trivial case. The method consists in replacing the real boundary conditions of a vibrating lattice by simplified ones, namely, the conditions of periodicity in a large parallelopipedic domain. There are several physical arguments in favour of this procedure: the real surface is unknown; it is very likely not smooth, but quite irregular and rough. We are not interested in properties of the surface, or in properties depending on the surface, but only in intrinsic properties of the matter forming the crystal. Further, mathematicians (Weyl, 1911, 12, 14, 15, and Courant, 1920) have proved that in a continuous medium the asymptotic distribution of vibrations for high frequencies does not depend on the shape of the surface nor on the boundary conditions. It is likely that the same should hold for a vibrating discontinuum. From the standpoint of physics, the cyclic condition is not without experimental confirmation. It is used in the electronic theory of metals, where it leads to a distribution of bands of electronic energy, called Brillouin zones, which are very similar to the frequency bands of the lattice vibrations. This band structure of electronic levels is the basis of the modern theory of mechanical and electrical properties of metals; it explains, for instance, the different types of conductivity in their relation to the periodic table of elements, and many other facts.

But I quite agree with Raman that the cyclic method is not proved, apart from the case of the linear monatomic lattice. Here the situation is this:—Let a chain of N equal particles (mass m) at equal distances a be coupled by quasi-elastic forces acting between neighbours only, equal to α per unit displacement; the ends may be either free or coupled to two fixed points at a distance a from

the ends by the same force α. Let the displacement of particle l for the normal mode j of frequency ω_j be u_l; then, omitting the time factor $\cos(\omega_j t + \epsilon_j)$, we have (Born and Karman, 1912):

Free ends:

$$u_l = u\cos(l-\tfrac{1}{2})\phi_j, \quad \omega_j = 2\sqrt{\left(\frac{a}{m}\right)}\left|\sin\frac{\phi_j}{2}\right|, \quad \phi_j = \frac{\pi j}{N}$$

Fixed ends:

$$u_l = u\sin l\phi_j, \qquad \omega_j = 2\sqrt{\left(\frac{a}{m}\right)}\left|\sin\frac{\phi_j}{2}\right|, \quad \phi_j = \frac{\pi j}{N+1}$$

$j = 1, 2, \ldots . N.$

This rigorous solution may be compared with that obtained with the cyclic condition, which is

$$u_l = ue^{il\phi_j}, \quad \omega_j = 2\sqrt{\left(\frac{a}{m}\right)}\left|\sin\frac{\phi_j}{2}\right|, \quad \phi_j = \frac{2\pi j}{N}, \quad j = 1, 2, \ldots . \frac{N}{2}.$$

In all cases the distribution of the frequencies over the scale of wave number (j-scale) is uniform; but in the total range of frequencies $\left(0 < \omega_j \leqslant 2\sqrt{\left(\frac{\alpha}{m}\right)}\right)$ there are apparently twice as many frequencies in the rigorous solution as in the cyclic solution. The reason is simply that in the latter case each solution is complex, hence represents really two solutions (corresponding to two independent running waves with opposite equal velocities), while the correct solution is one standing wave (or two opposite running waves with constant phase relation). The total number of frequencies is therefore exactly the same in both cases. For small N the cyclic spectrum is rather different from the real one; but for large N both tend to the same uniform density of frequencies.

This example shows only one branch and does not help to clarify the situation in the higher branches with which Raman's theory is concerned. I propose, therefore, to treat here another simple example, the di-atomic linear lattice. I shall show in the following section that in this case, also, the cyclic method leads, for large N, to the same result for both branches as the correct solution for the finite chain.

The case of a 3-dimensional lattice brings in a new feature, the shape of the boundary. Here a simple result can only be expected asymptotically for high wave numbers, as in the case of continous media.

Assuming that the uniform density of vibrations in the space of wave numbers (reciprocal space) is correct, there is no ambiguity in the theory of x-ray scattering. I shall, in the last section, give a short account of this theory and show where Raman's considerations * are inaccurate or incorrect.

§ 2. THE LINEAR DIATOMIC CRYSTAL

Let N atoms of mass m_1 and N atoms of mass m_2 (figure 1) form an equidistant alternating chain, which is an equilibrium configuration if all forces except those

Figure 1.

between first neighbours are negligible. If $u_1, u_2, \ldots u_N$ are the (longitudinal)

* I shall not use Raman's notation, but write his formulae in such a way that they can be readily compared with the general theory.

displacements of the first kind of atoms, $v_1, v_2, \ldots v_N$ those of the second kind, the equations of motion for small vibrations are

$$\begin{aligned}
&m_1\ddot{u}_1=\alpha(v_1-u_1), && m_2\ddot{v}_1=\alpha(u_2-v_1)-\alpha(v_1-u_1),\\
&m_1\ddot{u}_2=\alpha(v_2-u_2)-\alpha(u_2-v_1), && m_2\ddot{v}_2=\alpha(u_3-v_2)-\alpha(v_2-u_2),\\
&\quad\ldots\ldots\ldots\ldots && \quad\ldots\ldots\ldots\ldots\\
&m_1\ddot{u}_l=\alpha(v_l-u_l)-\alpha(u_l-v_{l-1}), && m_2\ddot{v}_l=\alpha(u_{l+1}-v_l)-\alpha(v_l-u_l),\\
&\quad\ldots\ldots\ldots\ldots && \quad\ldots\ldots\ldots\ldots\\
&m_1\ddot{u}_N=\alpha(v_N-u_N)-\alpha(u_N-v_{N-1}), && m_2\ddot{v}_N= \quad -\alpha(v_N-u_N).
\end{aligned} \qquad \ldots\ldots(1)$$

The difficulty of this problem lies in the deviation of the first and the last equation from the general form of all the rest; this deviation is the expression of the correct boundary conditions, namely, that the first and last particles are subjected to no external forces.

The cyclic device overcomes this difficulty by adding the missing terms, writing for the first and last equations

$$\begin{aligned}
&m_1\ddot{u}_1=\alpha(v_1-u_1)-\alpha(u_1-v_0), && \quad\ldots\ldots\ldots\ldots\\
&\quad\ldots\ldots\ldots\ldots && m_2\ddot{v}_N=\alpha(u_{N+1}-v_N)-\alpha(v_N-u_N),
\end{aligned}$$

and adding the condition that $v_0=v_N$, $u_{N+1}=u_1$. Then the finite chain can be extended to infinity on both sides by periodic repetition, so that the general conditions $u_l=u_{N+l}$, $v_l=v_{N+l}$ (which contain the two special ones) hold. The modified problem can be immediately solved.

I shall, however, give a rigorous solution of the equations (1). We consider a harmonic vibration with frequency ω, where all the u_l, v_l are proportional to $\exp(-i\omega t)$. With the abbreviations

$$\tfrac{1}{2}(m_1+m_2)=m, \qquad m\omega^2/2\alpha=\epsilon, \qquad \ldots\ldots(2)$$

the equations can be written

$$\begin{aligned}
&\left(1-2\frac{m_1}{m}\epsilon\right)u_1=v_1, && \left(1-\frac{m_2}{m}\epsilon\right)v_1=\tfrac{1}{2}(u_1+u_2),\\
&\left(1-\frac{m_1}{m}\epsilon\right)u_2=\tfrac{1}{2}(v_1+v_2), && \left(1-\frac{m_2}{m}\epsilon\right)v_2=\tfrac{1}{2}(u_2+u_3),\\
&\quad\ldots\ldots\ldots && \quad\ldots\ldots\ldots\\
&\left(1-\frac{m_1}{m}\epsilon\right)u_l=\tfrac{1}{2}(v_{l-1}+v_l), && \left(1-\frac{m_2}{m}\epsilon\right)v_l=\tfrac{1}{2}(u_l+u_{l+1}),\\
&\quad\ldots\ldots\ldots && \quad\ldots\ldots\ldots\\
&\left(1-\frac{m_1}{m}\epsilon\right)u_N=\tfrac{1}{2}(v_{N-1}+v_N), && \left(1-2\frac{m_2}{m}\right)v_N=u_N.
\end{aligned} \qquad \ldots\ldots(3)$$

We try to solve these equations by expressions of the form (omitting the time factor)

$$\begin{aligned}
u_l&=A_1\cos l\phi+A_2\sin l\phi,\\
v_l&=B_1\cos l\phi+B_2\sin l\phi,
\end{aligned} \qquad \ldots\ldots(4)$$

and substitute these first in the two equations with index l. We easily find

$$\begin{aligned}
\tfrac{1}{2}(u_l+u_{l+1})=\cos\phi/2\{&\cos l\phi(A_1\cos\phi/2+A_2\sin\phi/2)\\
&+\sin l\phi(-A_1\sin\phi/2+A_2\cos\phi/2)\},\\
\tfrac{1}{2}(v_{l-1}+v_l)=\cos\phi/2\{&\cos l\phi(B_1\cos\phi/2-B_2\sin\phi/2)\\
&+\sin l\phi(B_1\sin\phi/2+B_2\cos\phi/2)\}.
\end{aligned}$$

By equating the factors of $\cos l\phi$ and $\sin l\phi$ on both sides of these equations, four conditions are obtained:

$$\left(1-\frac{m_1}{m}\epsilon\right)A_1=\cos\phi/2(B_1\cos\phi/2-B_2\sin\phi/2),$$

$$\left(1-\frac{m_1}{m}\epsilon\right)A_2=\cos\phi/2(B_1\sin\phi/2+B_2\cos\phi/2),$$

$$\left(1-\frac{m_2}{m}\epsilon\right)B_1=\cos\phi/2(A_1\cos\phi/2+A_2\sin\phi/2),$$

$$\left(1-\frac{m_2}{m}\epsilon\right)B_2=\cos\phi/2(-A_1\sin\phi/2+A_2\cos\phi/2). \qquad \ldots\ldots(5)$$

These are 4 linear equations for A_1, A_2, B_1, B_2. The determinant of the 4th order is the square of a determinant of the 2nd order; each root is double, and therefore 2 of the 4 quantities A_1, A_2, B_1, B_2 can be chosen arbitrarily. One sees this easily by substituting, for instance, B_1, B_2 from the 3rd and 4th equation in the first two, which reduce to

$$\left(1-\frac{m_1}{m}\epsilon\right)\left(1-\frac{m_2}{m}\epsilon\right)A_1=A_1\cos^2\phi/2,$$

$$\left(1-\frac{m_2}{m}\epsilon\right)\left(1-\frac{m_1}{m}\epsilon\right)A_2=A_2\cos^2\phi/2.$$

Hence A_1, A_2 are indeterminate, and the 2nd order determinantal equation is

$$\left(1-\frac{m_1}{m}\epsilon\right)\left(1-\frac{m_2}{m}\epsilon\right)-\cos^2\phi/2=0; \qquad \ldots\ldots(6)$$

the solution of this quadratic equation is

$$\left.\begin{matrix}\epsilon^{(1)}\\ \epsilon^{(2)}\end{matrix}\right\}=\frac{m^2}{m_1m_2}\left[1\mp\sqrt{\left(1-\frac{m_1m_2}{m^2}\sin^2\phi/2\right)}\right], \qquad \ldots\ldots(7)$$

or, if we put

$$m_1=m(1+\mu), \qquad \mu=\tfrac{1}{2}\frac{m_1-m_2}{m_1+m_2},$$

$$m_2=m(1-\mu), \qquad \frac{m_1m_2}{m^2}=1-\mu^2, \qquad \ldots\ldots(8)$$

$$\left.\begin{matrix}\epsilon^{(1)}\\ \epsilon^{(2)}\end{matrix}\right\}=\frac{1}{1-\mu^2}[1\mp\sqrt{(\cos^2\phi/2+\mu^2\sin^2\phi/2)}]. \qquad \ldots\ldots(9)$$

We now substitute the expressions (4) into the first and last equation of the set (3); this gives

$$\left(1-2\frac{m_1}{m}\epsilon\right)(A_1\cos\phi+A_2\sin\phi)=B_1\cos\phi+B_2\sin\phi,$$

$$\left(1-2\frac{m_2}{m}\epsilon\right)(B_1\cos N\phi+B_2\sin N\phi)=A_1\cos N\phi+A_2\sin N\phi. \qquad \ldots\ldots(10)$$

Here we eliminate two of the constants, say A_1 and A_2, with the help of (5); then we obtain

$$\left(1-2\frac{m_1}{m}\epsilon\right)\left(1-\frac{m_2}{m}\epsilon\right)\frac{1}{\cos\phi/2}(B_1\cos\phi/2+B_2\sin\phi/2)=B_1\cos\phi+B_2\sin\phi,$$

$$\left(1-2\frac{m_2}{m}\epsilon\right)(B_1\cos N\phi+B_2\sin N\phi)$$

$$=\left(1-\frac{m_2}{m}\epsilon\right)\frac{1}{\cos\phi/2}[B_1\cos(N-\tfrac{1}{2})\phi+B_2\sin(N-\tfrac{1}{2})\phi]. \quad \ldots\ldots(11)$$

The first of these equations can be written

$$B_1\left\{\left(1-2\frac{m_1}{m}\epsilon\right)\left(1-\frac{m_2}{m}\epsilon\right)-\cos\phi\right\}$$

$$+B_2\left\{\left(1-2\frac{m_1}{m}\epsilon\right)\left(1-\frac{m_2}{m}\epsilon\right)\tan\phi/2-\sin\phi\right\}=0,$$

and with the help of (6) simplified to

$$B_1=B_2\frac{1-\frac{m_2}{m}\epsilon}{\frac{m_2}{m}\epsilon}\tan\phi/2. \quad \ldots\ldots(12)$$

The second equation (11) can be written

$$\cos N\phi\left\{B_1\frac{m_2}{m}\epsilon-B_2\left(1-\frac{m_2}{m}\epsilon\right)\tan\phi/2\right\}$$

$$+\sin N\phi\left\{B_2\frac{m_2}{m}\epsilon+B_1\left(1-\frac{m_2}{m}\epsilon\right)\tan\phi/2\right\}=0.$$

Here the coefficient of $\cos N\phi$ vanishes in virtue of (12), and that of $\sin N\phi$, namely (using (12) again)

$$B_2\left\{\left(\frac{m_2}{m}\epsilon\right)^2+\left(1-\frac{m_2}{m}\epsilon\right)^2\tan^2\phi/2\right\}\Big/\frac{m_1}{m}\epsilon,$$

does not vanish identically. Hence

$$\sin N\phi=0, \qquad \phi_j=\frac{\pi}{N}j, \qquad j=1, 2, \ldots\ldots N. \quad \ldots\ldots(13)$$

The range of the values of j is determined by the consideration that, according to (9), the range of ϕ for which the frequency assumes each possible value just once, is given by $0<\phi\leqslant\pi$.

This proves that the distribution of frequencies is the same (for each branch $\epsilon^{(1)}$, $\epsilon^{(2)}$) as in the case of a monatomic chain, namely uniform in the j-scale.

This rigorous solution may now be compared with that obtained from the cyclic conditions (Born and Goeppert-Mayer, 1933). One has in this case the complex solution

$$u_l=ue^{il\phi}, \qquad v_l=ve^{il\phi}; \quad \ldots\ldots(4')$$

the amplitudes u, v have to satisfy

$$u\left(1-\frac{m_1}{m_i}\epsilon\right)-v\tfrac{1}{2}(1+e^{-i\phi})=0,$$

$$-u\tfrac{1}{2}(1+e^{i\phi})+v\left(1-\frac{m_2}{m}\epsilon\right)=0; \quad \ldots\ldots(5')$$

the matrix is Hermitean, but the determinantal equation is the same as before, (6), namely,

$$\begin{vmatrix} 1-\frac{m_1}{m}\epsilon & -\frac{1}{2}(1+e^{-i\phi}) \\ -\frac{1}{2}(1+e^{i\phi}) & 1-\frac{m_2}{m}\epsilon \end{vmatrix} = \left(1-\frac{m_1}{m}\epsilon\right)\left(1-\frac{m_2}{m}\epsilon\right) - \cos^2\phi/2 = 0, \qquad \ldots\ldots(6')$$

and, therefore, again we reach the expression (9) for $\epsilon^{(1)}$, $\epsilon^{(2)}$.

The set of admissible values for ϕ is obtained from the condition of periodicity, which leads to

$$\phi_j = \frac{2\pi}{N} j, \qquad j = 1, 2, \ldots . \frac{N}{2} . \qquad \ldots\ldots(13')$$

This differs from (13), as the density of the ϕ_j values is only half of that of the rigorous solution. But as the solution (4') is complex, each value j corresponds to two real solutions, representing two independent waves of equal velocity in opposite directions. Each frequency is therefore to be counted twice, and the total number is the same as for the correct solution.

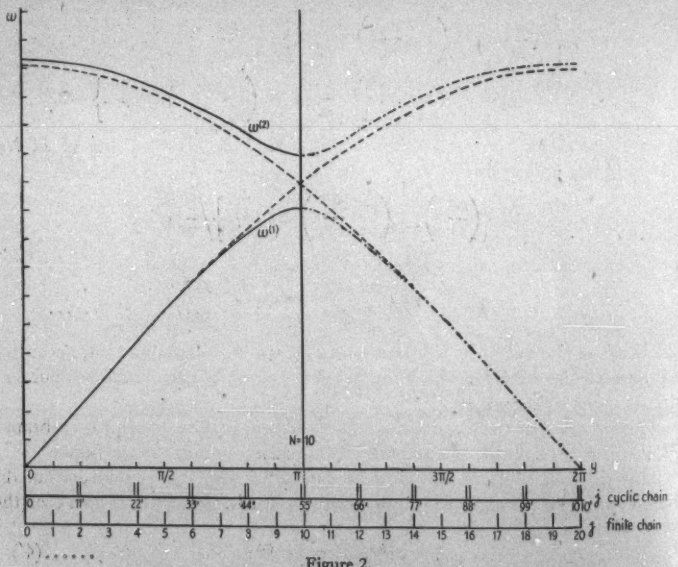

Figure 2.

The main point is the fact that the functions $\omega^{(1)}(\phi)$, $\omega^{(2)}(\phi)$ are exactly identical for the rigorous and the cyclic solutions. There are two branches, as illustrated in figure 2. This shows the well-known graph of the functions $\omega^{(1)}(\phi) = \sqrt{(2\alpha\epsilon^{(1)}/m)}$, $\omega^{(2)}(\phi) = \sqrt{(2\alpha\epsilon^{(2)}/m)}$ given by (9), and the ϕ_j-values, with $N = 10$, for the rigorous and the cyclic solution.

The dotted lines represent the case of equal masses, $\mu=0$, where the frequencies are

$$\omega^{(1)}=2\sqrt{\frac{a}{m}}|\sin\phi/4|, \quad \omega^{(2)}=2\sqrt{\frac{a}{m}}|\cos\phi/4|; \qquad \ldots\ldots(14)$$

these curves intersect at $\phi=\pi$, the end point of the domain of ϕ, which contains the whole spectrum just once. For different masses, $\mu\neq 0$, the two branches deviate from these curves with increasing ϕ and differ for $\phi=\pi$ by a finite distance. The upper branch $\omega^{(2)}$ corresponds in 3-dimensional lattices to the "optical" vibrations, to which Raman attributes the new x-ray reflections and which he supposes to be monochromatic. In fact, they are spread over finite frequency intervals. In the linear model the upper branch becomes monochromatic if $m_2 \ll m_1$; then an expansion of (9) with respect to m_2/m_1 leads to the approximate values

$$\omega^{(1)}=\sqrt{\frac{\alpha}{m_1}}|\sin\phi/2|, \quad \omega^{(2)}=\sqrt{2\frac{\alpha}{m_2}}, \qquad \ldots\ldots(15)$$

the second of which is constant. But even in this case Raman's assumption concerning the x-ray scattering cannot be justified, as I shall explain briefly in the last section.

The preceding considerations are an example of classical mechanics. As Raman very rightly insists that the diffuse x-ray spots are due to a quantum effect, it is desirable to formulate the results in such a way that they conform with orthodox quantum mechanics.

For this purpose the conjugate momenta p_l, p_l' of the displacements u_l, v_l must be introduced; the variables commute, except the pairs u_l, p_l and v_l, p_l', and we have, for instance,

$$u_l p_l - p_l u_l = \hbar i. \qquad \ldots\ldots(16)$$

Now we consider the functions (4) where A_1, A_2, B_1 can be expressed as multiples of B_2 (as explicitly given for B_1 by (12)), and determine B_2 by the normalization condition

$$\sum_l (m_1 u_l^2 + m_2 v_l^2) = 1. \qquad \ldots\ldots(17)$$

There are two such pairs of functions u_l, v_l for each integer j, corresponding to the two frequencies $\omega_j^{(1)}$, $\omega_j^{(2)}$; we write these

$$\begin{pmatrix} u_{lj}^{(1)} & v_{lj}^{(1)} \\ u_{lj}^{(2)} & v_{lj}^{(2)} \end{pmatrix}. \qquad \ldots\ldots(18)$$

If l and j assume the values 1, 2, ... N, these small matrices form a big matrix of order $2N$ which is orthogonal in the sense of the normalization (17).

We now introduce *normal coordinates* $\xi_j^{(1)}$, $\xi_j^{(2)}$ by the linear (orthogonal) transformation:

$$\begin{aligned} u_l &= \sum_j (u_{lj}^{(1)}\xi_j^{(1)} + u_{lj}^{(2)}\xi_j^{(2)}), \\ v_l &= \sum_j (v_{lj}^{(1)}\xi_j^{(1)} + v_{lj}^{(2)}\xi_j^{(2)}), \end{aligned} \qquad \ldots\ldots(19)$$

and the conjugate momenta $\eta_j^{(1)}$, $\eta_j^{(2)}$ by the same transformation of p_l, p_l'. Then the $\xi_j^{(k)}$, $\eta_j^{(k)}$, $(k=1, 2)$, satisfy the commutation laws

$$\xi_j^{(k)}\eta_{j'}^{(k')} - \eta_{j'}^{(k')}\xi_j^{(k)} = \delta_{jj'}\delta_{kk'}. \qquad \ldots\ldots(20)$$

The kinetic and potential energy

$$T=\tfrac{1}{2}\sum_{l=1}^{N}\left(\frac{1}{m_1}p_l^2+\frac{1}{m_2}p_l'^2\right),$$
$$U=\frac{\alpha}{2}\sum_{l=1}^{N}(v_l-u_l)^2+\frac{\alpha}{2}\sum_{l=1}^{N-1}(u_{l+1}-v_l)^2 \qquad \ldots\ldots(21)$$

are transformed into sums of squares

$$T=\tfrac{1}{2}\sum_{j=1}^{N}(\eta_j^{(1)2}+\eta_j^{(2)2}),$$
$$U=\tfrac{1}{2}\sum_{j=1}^{N}(\omega_j^{(1)2}\,\xi_j^{(1)2}+\omega_j^{(2)2}\,\xi_j^{(2)2}), \qquad \ldots\ldots(22)$$

where $\omega_j^{(1)}$, $\omega_j^{(2)}$ are the two branches of the frequency spectrum, defined by (9).

The dynamics of the crystal are described in quantum mechanics with the help of the Hamiltonian

$$T+U=H(\xi,\eta)=\sum_{j=1}^{N}\{H_j^{(1)}(\xi_j^{(1)},\eta_j^{(1)})+H_j^{(2)}(\xi_j^{(2)},\eta_j^{(2)})\}, \qquad \ldots\ldots(23)$$

where

$$H_j^{(k)}(\xi,\eta)=\tfrac{1}{2}(\eta^2+\omega_j^{(k)2}\xi^2), \qquad (k=1,2) \qquad \ldots\ldots(24)$$

is the Hamiltonian of a harmonic oscillator with the frequency $\omega_j^{(k)}$.

Analogous formulae will hold for any 3-dimensional lattice where l and ϕ represent triads of numbers and k may have more than two values.

§ 3. X-RAY SCATTERING

This section contains a short critical comparison of Raman's "theory of quantum reflections" with the correct quantum theory of scattering.

Raman starts with an expression for the amplitude of the scattered wave, of the form

$$E_0\,e^{i\omega t}\sum_l \alpha_l\,e^{i\Delta_l^0}\cdot e^{i\Delta_l'}; \qquad \ldots\ldots(25)$$

here E_0, ω are amplitude and frequency of the incident wave, α_l the polarizability of the atom l, $\Delta_l^0=\dfrac{2\pi}{\lambda}r_l\,.\,(s'-s)$, λ the wave length, r_l the position vector of the atom l, s and s' the unit vectors in the direction of the wave normals of the incident and scattered beam. The last factor expresses the influence of the vibrations; Raman assumes that the Δ_l' are proportional to the displacements of the individual atoms and puts $\Delta_l'=u_l\cos(\omega_l t+\epsilon_l)$. This is not correct as the atoms are coupled; one has to put

$$\Delta_l'=\sum_j u_{l_j}\xi_j, \qquad \ldots\ldots(26)$$

where ξ_j are the normal coordinates, which perform harmonic vibrations. Correcting this point, we write

$$\xi_j=\cos(\omega_j t+\epsilon_j) \qquad \ldots\ldots(27)$$

and expand

$$e^{i\Delta_l'}=1+i\,\Delta_l'=1+i\sum_j u_{l_j}\cos(\omega_j t+\epsilon_j). \qquad \ldots\ldots(28)$$

If the cos is replaced by exponential functions of $\pm i(\omega_j t+\epsilon_j)$ and (28) substituted in (25) we see that, apart from a term with unchanged frequency, two terms with modified frequencies $\omega+\omega_j$ and $\omega-\omega_j$ and an arbitrary phase

are obtained. These terms represent, according to Raman, the new quantum reflections,† and all his further conclusions are derived from these (*Symposium*, p. 338). But these formulae are quite classical.

The correct procedure according to quantum mechanics consists in considering the vibrating lattice in two vibrational states and forming the matrix element corresponding to the transition $n \to n'$; if the α_l are considered as independent of the vibrations (neglecting the Raman effect proper ‡) only the Δ_l' depend on the ξ_j and hence on n, n'. Thus

$$E_0 e^{i\omega t} \sum_l \alpha_l e^{i\Delta_l^0} \left(e^{i\sum_j u_{lj} \xi_j} \right)_{nn'} e^{i(\omega_{nn'} t + \delta_{nn'})}, \qquad \ldots\ldots(29)$$

where $\hbar\omega_{nn'}$ is the energy difference between the states n, n' and $\delta_{nn'}$ an arbitrary phase. This shows that there are, apart from the unchanged (coherent) wave ($n=n'$, $\omega_{nn}=0$), a set of incoherent waves with changed frequencies $\omega+\omega_{nn'}$, one for each possible transition.

Actually this change of frequency is quite negligible in view of the enormous size of the X-ray photon $\hbar\omega$ as compared with infra-red quanta $\hbar\omega_{nn'}$. The important point is the incoherence, which implies that the intensity is obtained by adding the squares of the moduli of the individual wavelets. The total intensity is therefore obtained by multiplying the squared modulus of (29) by the Boltzmann factor corresponding to the initial state n, and summing first over all transitions from any other state n' to n, and then over all n. The first of these summations can be rigorously performed, since (with real eigenfunctions) for any matrix $f(n, n')$ one has

$$\sum_{n'} |f(n, n')|^2 = |f|^2(n, n').$$

In this way the intensity is found to be

$$I = I_0 \sum_{ll'} \alpha_l \alpha_l^* e^{i(\Delta_l^0 - \Delta_{l'}^0)} \prod_j \text{mean}\,(e^{i\mu_j^{ll'} \xi_j}), \qquad \ldots\ldots(30)$$

where $\mu_j^{ll'} = u_{lj} - u_{l'j}$ and

$$\text{mean}\,(e^{i\mu\xi}) = \sum_n (e^{i\mu\xi})_{nn'} \frac{e^{-\epsilon_n/kT}}{\sum_n e^{-\epsilon_n/kT}}. \qquad \ldots\ldots(31)$$

Here n means the quantum number of a single oscillator (amplitude ξ), and $\epsilon_n = \hbar\omega(n+\frac{1}{2})$ its energy.

This average of a harmonic function of the oscillator amplitude seems to me the central problem of the theory, as all consequent operations are of a purely geometric character. But the determination of this mean (31) is not quite trivial and has been the source of much confusion.

Debye (1913, 14) replaced $e^{i\mu\xi}$ by $1+i\mu\xi-\frac{1}{2}\mu^2\xi^2+\ldots$ and taking the mean term by term [mean $(\xi)=0$, mean $(\xi^2)=\bar{\epsilon}/\omega^2$, where

$$\bar{\epsilon} = \hbar\omega \left(\frac{1}{2} + \frac{1}{e^{\hbar\omega/kT}-1} \right) = \frac{\hbar\omega}{2} \coth \left(\frac{1}{2} \frac{\hbar\omega}{kT} \right) \qquad \ldots\ldots(32)$$

† As a matter of fact, Raman does not use the expansion (28) from the start, but a little more general expansion into a series of Bessel functions; but later he uses only the first terms of the power series of these functions, which is equivalent to the expansion (28).

‡ This effect has been considered in one of my papers quoted, at least for the perfectly symmetrical modes which do not produce depolarization.

is Planck's oscillator energy] he obtained $1-\frac{1}{2}\mu^2\bar{\epsilon}/\omega^2+\ldots$ and replaced this by an exponential function,

$$\text{mean}\,(e^{i\mu\xi}) = e^{-\frac{1}{2}\mu^2\bar{\epsilon}/\omega^2}. \qquad \ldots\ldots(33)$$

Waller (1925) devoted an appendix of his important paper to an attempt at improving this procedure, but succeeded only for high temperatures (Boltzmann statistics). A rigorous proof was given by Ott in 1935, and a simpler one in the first of our papers (Born and Sarginson, 1941).

The correct derivation of (33) is not an unnecessary refinement,—for the exponent becomes infinite when $\omega\to 0$; hence Debye's expansion is valid only if very small values of ω can be excluded. But this is impossible, as the product appearing in (30) contains factors corresponding to every frequency, including those of the acoustical branches which approach zero; for these the single factors of the form (33) cannot be expanded.

But if the product is transformed,

$$\prod_j \text{mean}\,(e^{i\mu_j^{k'}\xi_j}) = \exp\left(-\tfrac{1}{2}\sum_j \mu_j^{k'}\bar{\epsilon}_j/\omega_j^2\right) = \Pi_{k'}; \qquad \ldots\ldots(34)$$

the sum in the exponent converges, even for the acoustical branches. The result can then, of course, be expanded into powers of the small quantities μ:

$$\Pi_{k'} = 1-\tfrac{1}{2}\sum_j (\mu_j^{k'})^2\,\bar{\epsilon}_j/\omega_j^2+\ldots. \qquad \ldots\ldots(35)$$

Substituting this in (30) we obtain two terms, one representing the Laue scattering, the other the influence of the thermal motion:

$$I = -I_0\cdot\tfrac{1}{2}\sum_j \frac{\bar{\epsilon}_j}{\omega_j^2}\sum_{k'}\alpha_l\alpha_l^*(\mu_j^{k'})^2\,e^{i(\Delta_l^0-\Delta_{l'}^0)}. \qquad \ldots\ldots(36)$$

The further development of this formula for a lattice is a straightforward process which will not be explained here. I have dwelt on the question of Debye's expansion in some detail as several modern authors (Zachariasen, 1940, 1; Jahn, 1941, 2) have failed to recognize the difficulty, and also because this appearance of ω^2 in the denominator is connected with Raman's erroneous conclusions.

Raman wishes to prove that the acoustical branch of the spectrum cannot produce sharp spots. Squaring his classical expression for the scattered amplitude, he identifies $\frac{1}{2}\omega^2u^2$ with $\boldsymbol{kT}$; then he replaces ω by $2\pi c/\lambda$ (c = velocity of sound, λ = wave-length) and finds the intensity proportional to $\boldsymbol{kT}\lambda^2$, a smooth function which cannot give rise to sharp maxima, but only to a diffuse background. But this is not correct. There is no constant velocity of elastic waves in the crystal, but a kind of dispersion. For a monatomic linear chain the formula is given in the introduction; it can be written

$$\omega = 2\sqrt{\frac{\alpha}{m}}\left|\sin\phi/2\right| = 2\sqrt{\frac{\alpha}{m}}\left|\sin\frac{\pi a}{\lambda}\right| = 2\sqrt{\frac{\alpha}{m}}\left|\sin\frac{\pi q}{b}\right|;\ b=\frac{1}{a}; \qquad \ldots\ldots(37)$$

here $q=1/\lambda$ is the wave number, $b=1/a$ the lattice constant of the reciprocal lattice, and

$$\phi = \frac{2\pi q}{\lambda} = \frac{2\pi q}{b}. \qquad \ldots\ldots(38)$$

The corresponding expressions for a diatomic chain (§1, equation (9)) are

similar periodic functions of $\phi/2=\pi q/b$. It is true that all frequencies and motions of the particles can be obtained by restricting ϕ to the interval $0\leqslant\phi\leqslant\pi$ (hence $0\leqslant q\leqslant\frac{1}{2}b$, or $2a\leqslant\lambda\leqslant\infty$); but each of these waves is the longest sample in a whole set of "equivalent" waves, given by ϕ, $\phi\pm\pi$, $\phi\pm 2\pi$, ... It is necessary to admit these shorter waves in order to express in a simple form the interference condition or, what is the same thing, the conservation law for momentum, according to de Broglie.

The discussion of the expression (36) for the intensity gives the result that enhancement of scattered wavelets from different lattice points by interference takes place if the wave vectors Q, Q' of the incident and scattered radiation and the wave vector q of an elastic wave in the crystal satisfy the condition

$$Q'-Q=q. \qquad \ldots\ldots(39)$$

The intensity can then be expressed in the form

$$I=S(Q'-Q), \qquad \ldots\ldots(40)$$

where $S(q)$, the scattering power, is a function in the reciprocal-lattice co-ordinates (q_1, q_2, q_3). To illustrate this, let us consider the reflections by a definite set of parallel equidistant lattice planes, and assume that these planes vibrate as a whole normal to themselves.

These vibrations will be the same as those of a chain of equal equidistant particles, and the frequency given by (37).

The interference condition (39) reduces to

$$Q(\sin\vartheta'-\sin\vartheta)=q, \quad \cos\vartheta'-\cos\vartheta=0, \quad \text{hence } \vartheta'=-\vartheta, \qquad \ldots\ldots(41)$$

where $Q=1/\Lambda$, the wave number of the x rays, $q=1/\lambda$, that of the elastic waves. It is clear that q cannot be restricted to the interval $0\leqslant q\leqslant b/2$. Taking Raman's approximate expression for the mean amplitude, the scattered intensity will be

$$I=S(2Q\sin\vartheta), \qquad \ldots\ldots(42)$$

where

$$S(q)=\frac{kT}{\dfrac{4\alpha}{m}\sin^2(\pi q/b)} \qquad \ldots\ldots(43)$$

is the scattering power, a function distributed over the whole reciprocal space q, which is condensed around the points of the reciprocal lattice,

$$q=0,\ b,\ 2b,\ 3b,\ \ldots.$$

where it has sharp (infinite) peaks. These correspond to the Bragg reflections, as $2Q\sin\vartheta=nb$ is the same as $2a\sin\vartheta=n\Lambda$ (figure 3). If all vibrations in 3 dimensions are taken into account, the expression $S(q)=S(q_1, q_2, q_3)$ is more complicated, but the main features are the same: it is a function in the reciprocal space additively composed of contributions of the different branches of the elastic spectrum. The terms corresponding to the acoustical branches have sharp peaks (infinities) at the points of the reciprocal lattice (corresponding to the Laue spots), because the frequency approaches zero. If the scattering power were completely condensed at these peaks there would be only the Laue spots; but as it is spread around them in virtue of the temperature motion, there is an additional scattering, not confined to the selected directions (for given wave-length) of the Laue spots, but increasing in intensity on approaching these directions. The maxima are observed as extra spots. Their intensity depends very strongly on the wave-length and direction of the incident beam with respect

to the lattice, since the domains of scattering power have characteristic anisotropic shapes different for different Laue spots. I shall return to this question later. Here we stress the point that the maxima are produced by the acoustical branches of the vibrational spectrum.

The high-frequency branches are always well above the zero level and will therefore contribute only a diffuse background with weak maxima midway between Laue points, traces of which seem to have been found by Lonsdale and Smith.†

The part played by the low- and high-frequency branches is just the opposite to that which Raman supposes.

For the high-frequency branches, Raman makes an attempt to introduce quantum theory in order to get the dependence on temperature. His reasoning is rather strange. He distinguishes two cases. If the number of vibrational quanta is diminished by the incident radiation, he assumes the energy given by the Planck formula without zero energy; but if this number is increased he adds to this $\hbar\omega$ (twice the zero energy). Then he adds these values and obtains an expression which is in fact $2\bar{\epsilon}$, where $\bar{\epsilon}$ is the Planck formula (32) with zero

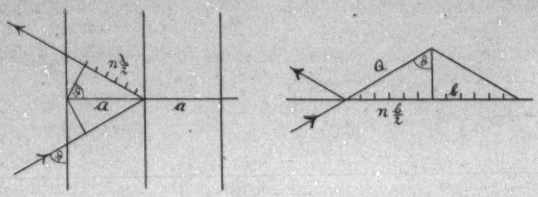

Figure 3.

energy (*Symposium*, p. 350). The rigorous theory leads to the same temperature factor for all frequencies, including the low branches. The experiments of Venkateswaran (*Symposium*, p. 387 ff.), which are supposed to confirm this dependence on temperature, were made on extra spots well separated from the corresponding Laue spots; this means that the corresponding scattering frequency is rather far above the zero limit of the acoustical branch and of the same order of magnitude (infra-red) as the optical branches. All the experiments showed was that for carborundum the oscillations responsible for the extra spots were of higher frequency than those for a soft organic crystal, a result which the theory of lattice dynamics undoubtedly predicts, because of the difference of quasi-elastic force in the two substances. These measurements cannot be claimed as a confirmation of Raman's theory.

The most condensed formulation of the result of the thermal theory is the following one‡:—The potential energy of the mutual forces between the lattice points is a quadratic form in terms of the displacements; for harmonic waves, the matrix of coefficients is a function of the wave numbers or of ϕ. In the case of a diatomic linear lattice (§2) we have, for instance,

$$D(\phi)=2\alpha\begin{pmatrix} 1 & -\frac{1}{2}(1+e^{-i\phi}) \\ -\frac{1}{2}(1+e^{i\phi}) & 1 \end{pmatrix}, \qquad \ldots\ldots(39)$$

† According to private information.

‡ Materially contained in Waller's dissertation; the particular formulation with matrix functions is given in my last paper.

which is easily recognized as the matrix of the coefficients of the equations (5′).

The scattering power for a lattice composed of different atoms is also a quadratic form; the coefficients refer to the interaction of the pairs of different atoms and are also functions of ϕ. Let $S(\phi)$ be this scattering matrix. Then the result of the theory can be expressed in the form

$$S(\phi) = \frac{\hbar}{2} D^{-\frac{1}{2}}(\phi) \coth\left(\frac{\hbar}{2kT} D^{\frac{1}{2}}(\phi)\right) = kTD^{-1}(\phi) + \ldots . \qquad \ldots\ldots(40)$$

The scattering matrix $S(\phi)$ is a function of the dynamical matrix $D(\phi)$, and just the same function that, according to (32), $\bar{\varepsilon}(\omega)/\omega^2$ is of ω^2. Matrix equations like this are typical of quantum mechanics and could never be obtained by methods such as are used by Raman. The formula (40) may become of far-reaching importance, as it allows us to calculate $D(\phi)$ in terms of $S(\phi)$, and hence to determine the dynamical structure of the lattice from photographs of the extra spots. At present no quantitative data are available for this purpose. But the theory has been confirmed by considering the neighbourhood of the Laue spots, where the first term of the expansion, given by (40), is predominant and can be expressed with the help of the elastic constants. These formulae have been independently developed by Zachariasen (1940, 1), Sarginson (1942) and Jahn (1941, 2). The scattering power can be considered as condensed in regions surrounding the points of the reciprocal lattice, and Jahn has calculated the *iso-diffusion* surfaces. He found that for cubic crystals with marked elastic anisotropy, these surfaces are very far from being spherical, but have tentacles stretching out in different directions, and different for each lattice point. Knowing these surfaces, it is easy to find the scattered intensity with the help of Ewald's sphere of reflection (Ewald, 1913). This leads to characteristic differences for the intensities of the extra spots in the vicinity of different Laue spots, strongly dependent on the direction and wave-length of the incident beam. These predictions of the theory have been strikingly confirmed by experiments of Lonsdale and Smith (1942). Zachariasen also found good agreement of his formulae with observations (1940, 1).

Raman tries to explain the anisotropy of scattering power, deduced from the observations of his collaborators, by assuming that his monochromatic waves are propagated in selected directions. Rama Pisharoty (*Symposium*, pp. 377, 435) has carried out such calculations, but the assumptions made are rather arbitrary and the results not in good agreement with the facts (Lonsdale and Smith, 1942).

Finally I wish to mention another argument brought forward by Raman in favour of his assumption of monochromatic infra-red vibrations. His collaborator, Bisheshwar Dayal (*Symposium*, p. 421), has carried out calculations of the specific heat of metals in order to show that these cannot be represented by Debye curves, but that Einstein terms have to be added. This is quite true; the suggestion, however, is not new but already contained in my book *Dynamik der Kristallgitter* (1915) (formula 200, p. 77). As the optical branches are rather narrow, I showed that for quantities like the specific heat or the thermal expansion coefficient (which are average values over the whole spectrum) they may be

replaced by monochromatic vibrations. This fact in no way supports Raman's hypothesis.†

§ 4. CONCLUSION

I wish to add a personal remark. It was Raman's first publication on the new scattering effect which directed my attention to it. His striking observations were obviously directed by his theoretical ideas. A theory which leads to a series of good experiments has fulfilled its first task. But its permanent value depends on the question whether it can be built into the system of well-established facts, and whether its predictions are confirmed by independent experiments. I tried to reconcile Raman's ideas with the results of quantum mechanics and lattice theory; but he, unfortunately, insists on his formulations. The present paper is intended to show why this is impossible. Scattering of x rays by atoms is well inside the boundary of established knowledge, not on the fighting front, like nuclei, mesons, etc., and it is extremely unlikely that anything quite unexpected should happen. Therefore Raman's expectations go too far. On the other hand, the story of the development of this subject is not very glorious for theoretical physics. It is rather similar to that of the optical Raman effect. Here, as well as there, the complete theory was given long before the phenomenon was observed; but in both cases the discussion of the formulae was so imperfect that no real predictions were made and no hints given to the experimenter. Yet after the discovery of the optical Raman effect the connection between observation and theory was established at once and acknowledged by Raman himself. May these pages help to produce the same effect for the x-ray scattering.

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† When this MS. was just finished there appeared in the *Proc. Ind. Acad. Sci.* a new symposium of papers on the thermal energy of crystalline solids, in which this hypothesis is expanded and supported by experimental investigations on specific heat. My critical remarks are in no way affected by these new papers.

NOTE ON RAMAN'S THEORY OF THE SPECIFIC HEAT OF SOLIDS

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ABSTRACT. Raman's version of the theory of the specific heat of solids is examined; it is shown that the existing (lattice) theory of specific heat gives better agreement with experiment.

IN a recent publication, Raman (1941) has proposed a reformulation of the theory of the specific heat of solids, rejecting both the Debye theory and the lattice theory of specific heats, (cf. Born, 1923). Raman's theory replaces the (in the main) continuous vibrational spectrum of the current theory by a few discrete lines—the specific heat being therefore calculated from a sum of a few Einstein specific-heat functions.

The arguments which led Raman to the rejection of lattice theory are of a purely qualitative nature; these have been dealt with by Born (1942).* This note is concerned with the results obtained, and to be expected, from Raman's theory.

In the majority of cases in which the theory is applied by Raman's collaborators (Norris, Dayal, Anand, Venkateswaran, 1941), the frequencies of vibration of the crystal considered are obtained "from a perusal of the specific-heat data"; the agreement obtained with experiment does not, therefore, prove more than that a suitable sum of Einstein functions can give a good fit to the specific-heat data for a solid. A very good demonstration of this fact was given, in 1911, by the success of the Nernst-Lindemann formula.

In the particular case of rocksalt (Venkateswaran, 1941) the frequencies, with one exception, were obtained from the more or less clearly defined peaks in the Raman spectrum, on the assumption that these peaks are octaves of the required lattice vibrations. *The remaining frequency is assumed.* The frequencies for sylvine (Venkateswaran, 1941) were all taken to be 0·78 of those of rocksalt. The resulting specific heats "agree reasonably well with experimental results", and it is concluded "the investigation thus clearly demonstrates that the present approach to the theory of specific heat should replace the earlier ones due to Debye, Born and others".

No account is given in the investigation of the results of lattice theory; in view of the importance of any new theory of specific heat, it seems desirable that such a comparison should be made. This is done below (table 1).

The experimental results are due to Clusius and Perlick (1934) (for rocksalt),

* I am indebted to Professor Born for the information that a paper on this point is in progress of publication in the *Proceedings of the Physical Society*. (See this Part, p. 362.—ED.)

and to Keesom and Clark (1935) (for sylvine). Specific heats on the basis of lattice theory have been calculated by Kellermann (1941) and Iona (1941) for rocksalt and sylvine, respectively. It should be noted that there are no adjustable constants in the lattice theory.

Table 1. Specific heats of rocksalt and sylvine

$T°$ (K.)	C_v (expt.)	C_v (lat. theory)	C_v (Raman's theory)
	Rocksalt		
10	0·0326	0·0328	0·036
20	0·310	0·317	0·28
30	1·150	1·154	0·96
40	2·380	2·380	2·04
	Sylvine		
2·99	0·00206	0·0021	0·0016
4·01	0·0047	0·0049	0·0046
6·52	0·0191	0·0227	0·0219
8·00	0·046	0·043	0·043
10·06	0·084	0·087	0·0907

Judging solely by the agreement between theory and experiment, it is difficult to see any superiority on the part of Raman's theory.

There is a further point on which Raman's theory can be tested. The lattice theory of solids (Born, 1923) shows that the specific heat at very low temperatures can be calculated from the elastic constants. On Raman's theory, the specific heat at low temperature will depend on certain low-frequency lattice vibrations and *not* on the magnitudes of the elastic constants. This is, therefore, a point on which the theories disagree, and one which can be tested by reference to experiment.

Raman does consider the question briefly in his discussion of the Debye theory (Raman, 1941, p. 463), but dismisses the agreement as unimportant—"as was pointed out in Einstein's earliest papers, however, the existence of approximate relations between the atomic frequencies and elastic constants is indicated by elementary considerations".

One would not expect "approximate relations" to lead to reasonably good agreement in all cases in which a real test is possible. There are only a few cases in which the specific heat has been measured to sufficiently low temperatures and for which, in addition, elastic data are available. The most important of these are sylvine and rocksalt, the thermal data for which have been quoted above; the elastic data have been given by Durand (1936).

The comparison is made in terms of the constant θ calculated independently from the thermal and the elastic data; the temperature at which the comparison is made is 10° K. for NaCl (the lowest temperature available) and 2·99° K. in the case of KCl.

Table 2

	θ (sp. heat)	θ (elastic)
NaCl	230	246
KCl	308	320

The agreement is much closer than would be expected from an "approximate

relationship", and there are reasons for believing that the agreement is better than is indicated in table 2 (cf. Blackman, 1942).

A further case which can be cited is that of zinc, for which a value of θ (elastic) of 320 is obtained (cf. Eucken, 1929). The value of θ (sp. heat) is as low as 195 at 20° K., but rises steeply at lower temperatures (Keesom and v. d. Ende, 1932), and if the electronic specific heat is allowed for, eventually reaches a value of about 310 at 4° K. This is a particularly interesting case because of the large difference between the value of θ (sp. heat) at 20° K. and at 4° K.

The evidence presented above points to a very close correspondence between lattice theory and experiment. In view of this, quite apart from other reasons, the claim that Raman's theory "should replace the earlier ones by Debye, Born and others" seems, to put it at its highest, somewhat premature.

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NOTE ON THE COMPARISON OF THE SUBSIDIARY MAXIMA IN ELECTRON DIFFRACTION AND X-RAY DIFFRACTION PATTERNS FROM SINGLE CRYSTALS*

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ABSTRACT. The occurrence of diffuse bands in electron diffraction and their apparent non-appearance in x-ray diffraction is accounted for by differences in wavelength, intensity, crystal size, etc. Under suitable conditions it is expected that they may be observed with x rays.

A qualitative comparison is made of the Faxén-Waller theory, used to explain extra spots in the x-ray diffraction pattern, with the hypothesis advanced to account for the presence of diffuse bands. The former is in many respects equivalent to assuming

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approximate coherence in thermal vibrations over very limited regions of the crystal. If these regions shrink to unit-cell dimensions, the molecules therein vibrate very nearly independently, giving rise to diffuse bands, in addition to the usual Laue or Bragg spot patterns.

§1. INTRODUCTION

In the study of single crystals of some organic compounds by electron diffraction, we (Charlesby, Finch and Wilman, 1939) have observed very diffuse maxima, in addition to the normal Laue spot pattern. These maxima are related to the orientation of the molecules of the crystal relative to the incident beam, and their appearance can best be explained in terms of thermal motion. Assuming that groups of atoms (molecules) vibrate independently of their neighbours, the expression derived for the diffracted intensity was found to be

$$I \propto (A^2+B^2)\frac{\sin^2 M_1 h\pi}{\sin^2 h\pi}\cdot\frac{\sin^2 M_2 k\pi}{\sin^2 k\pi}\cdot\frac{\sin^2 M_3 l\pi}{\sin^2 l\pi}\overline{(\cos\phi)^2} + N\Sigma_p(A_p^2+B_p^2)(1-\overline{\cos\phi}^2).$$

The first term is the usual expression for the Laue spots modified by the structure factor and by a temperature factor $\overline{(\cos\phi)^2}$, the value of which decreases as the angle of diffraction increases. The other term corresponds to the diffuse maxima, the intensities of which are modified by the structure factor of each independent group and by a temperature factor, which increases with the distance from the central spot. If, moreover, we assume that the restoring force on any molecule is proportional to the displacement, a more precise expression can be obtained for $\overline{(\cos\phi)^2}$, viz.

$$\overline{(\cos\phi)^2} = \exp.\{[-16\pi^2\sin^2\theta/\lambda^2](\boldsymbol{k}T/f)\},$$

where f is the force constant, 2θ the angle of diffraction and the other terms have their usual significance. These diffraction maxima are of considerable importance in the elucidation of the structure of organic compounds, and it is surprising that no similar phenomenon has so far been observed in X-ray work.

This failure can be attributed to several reasons:—

1. *Difference in wave-length*

In electron diffraction the wave-length used is of the order of 0·05 A. In Robertson's work (1933) on anthracene the Cu Kα wave-length of 1·54 A. was used. The diffraction maxima occur approximately at angles 2θ defined by the equation

$$2d\sin\theta = n\lambda.$$

In molecules of the type of anthracene, the maximum effective grating spacing is 1·22 A., although less intense maxima occur at spacings corresponding to 2·31 A. The first-order diffraction maxima would then appear at an angle 2θ such that

$$\sin\theta = \frac{\lambda}{2d} = \frac{1\cdot54}{2\times1\cdot22} = 0\cdot63.$$

This implies that the angles of incidence and reflection from the corresponding grating spacings are equal. If this is not the case, the diffuse maxima occur at greater angles.

Robertson's experiments extend to angles 2θ such that $\sin\theta = 0{\cdot}767$ (corresponding to the 019 diffractions), but this is an unfavourable direction for the observation of diffuse maxima. More favourable conditions prevail when the crystal is oriented to obtain the $40\bar{9}$, $40\,\bar{1}0$, $60\bar{9}$ and $60\,\bar{1}0$ diffractions, when the orientation of the molecule is such as to present the maximum effective grating spacing. The corresponding values of $\sin\theta$ observed by Robertson were 0·620, 0·690, 0·658, 0·709 respectively, and these appear to be the highest values of $\sin\theta$ examined with this position of the molecule relative to the beam. Thus, even in the most favourable case, the first-order diffuse bands would be barely visible at the edge of the photographic plate, possibly further decreased in intensity by the oblique incidence. Higher orders, which are relatively more intense, would not appear. The less intense subsidiary maxima, corresponding to a minimum effective spacing of 2·31 A., should, however, be observable. As they are of much lower intensity and, moreover, are greatly weakened by the thermal factor, they may readily be overlooked.

In our electron-diffraction patterns, the maximum value of $\sin\theta$ observable on the plate was greater than 1/15, so that the third order could be recorded if the intensity were sufficient.

The absence of the zero-order reflection still remains to be explained. This order would be evidenced by a diffuse band surrounding the undeviated beam. According to the theory mentioned above, the temperature factor is such that this maximum should be well-nigh eliminated. It seems probable that any other explanation for the diffuse maxima would lead to a somewhat similar result. Unfortunately, the electron-diffraction pattern near the undeviated beam is blackened by inelastically scattered electrons, and observation is difficult; nevertheless it does appear that some such decrease takes place in its neighbourhood. The corresponding increase in intensity with angle of deviation, deduced from the formula, can be readily observed.

2. *Difference in relative intensities*

Compare the relative intensities of diffuse maxima and spot patterns obtained by the x-ray and electron-diffraction methods. In the former, the exposures are generally arranged to give suitable blackening of the Bragg spots, on which the analysis is based. In the latter case, most of the spots observed are Laue spots and only two of the three Laue conditions are accurately fulfilled. The very intense electron beam and its greater scattering ensure that a few seconds exposure leads to suitable blackening of these relatively weaker spots, and in most cases to considerable over-exposure of the few Bragg reflections. In electron diffraction it is found that a correct exposure for the Laue-spot pattern gives satisfactory intensities for the diffuse bands. In x-ray work one would therefore require a considerable over-exposure of the Bragg spots before the diffuse bands became visible. It is only recently that long exposures have been used to study the x-ray type of extra spots; thus the failure to observe diffuse bands is understandable.

This argument assumes, of course, that the relative intensities of the diffuse maxima and Bragg spots are independent of crystal size. We formerly considered (Charlesby, Finch and Wilman, 1939) that the maximum intensity

in a diffuse band is proportional to N, the number of unit cells in the crystal, whereas the intensity maximum of a Bragg spot is proportional to N^2; thus the diffuse maxima would be relatively more prominent in small crystals quite apart from the considerations outlined above. This statement appears to hold for our electron-diffraction patterns, but requires further qualification.

The intensity distribution in a spot depends not only on the Laue factors of the form $(\sin^2 M_1\pi h)/\sin^2 \pi h$, but also on other factors such as beam divergence and width. The Laue zones due to atom rows which are not too nearly parallel to the incident beam are generally so sharp that the spot size is essentially determined by the other factors involved. An increase in M_1, the number of unit cells in this direction (assumed already large), will only modify the form of the intensity distribution in the spot to a very slight extent. The intensity maximum of any given spot is in effect proportional to M_1.

When considering thick crystals a similar state of affairs holds for all directions in the crystal, so that the intensity is proportional to the product $M_1M_2M_3$, i.e. N. On the other hand, with thin crystal sheets, nearly perpendicular to the beam, M_1 is small for atom rows parallel to the beam; and for the range of diffracted beams recorded, the corresponding index h is always relatively small. A wide maximum occurs in the Laue factor and the reciprocal-lattice point is elongated in the direction normal to the sheet. This is evidenced in electron diffraction by a very wide Laue zone. As M_1 is increased, the intensity of spots near the maximum of the Laue zone increases as M_1^2, and at the same time the width of the Laue zone shrinks. In these thin specimens, therefore, the ratio of maximum spot intensity/maximum diffuse band intensity is proportional to thickness. The transition between the two forms of variation occurs for thicknesses such that the spot radius determined from the Laue conditions (i.e. $\sim 1/M_K$ of the distance between reciprocal lattice spots in the K direction) equals that inherently due to other causes. In electron diffraction this thickness may be estimated to be about 10^4 A.

Summarizing, the intensity of the diffuse bands should be proportional to the number of unit cells, N, whereas the intensity of a spot near the centre of a Laue zone (electron diffraction) varies as $M_1^2M_2M_3$ or NM_1 (where M_1 is the number of unit cells in a row nearly parallel to the incident beam). In X-ray work the observed Bragg-spot intensity varies as $M_1M_2M_3(=N)$. The ratio of the intensities of the diffuse bands to observed spots is then inversely proportional to thickness in electron diffraction, and is independent of thickness in X rays. Beam divergence in X rays will not affect this relationship. Similar conclusion can also be reached if one assumes the crystal under examination to consist of mosaic blocks, the dimensions of which are much smaller than, but independent of, the size of the crystal as used in X rays. In electron diffraction, in view of the thickness of the specimens used, the mosaic structure will occur in the plane of the film, but not at right angles to it.

3. *Other effects*

The relative increase in intensity of diffuse maxima in regions remote from the central spot can be readily seen in electron-diffraction patterns. If the bands due to only one anthracene molecule in the unit cell are considered, the

number of principal maxima visible throughout the plate is eighteen up to the second order and thirty-six up to the third order. The zero order is eliminated by the thermal factor. There are, moreover, twice as many secondary maxima, whose intensity is 54/196 that of the primary maxima. These maxima placed in regular array are far more readily observed than the few which might appear in X-ray patterns (using a wave-length of 1·54 A.) near the edge of a steeply inclined plate. This difference will be accentuated by the relatively large angular spread of each diffuse band, caused by the very limited extent of the molecular grating. This difference in scale would then give rise to bands, each extending over one quarter of the pattern. It is doubtful whether these bands could be observed above the general background of the Weissenberg photographs used by Robertson.

It has also been suggested that the diffuse bands may be due to some surface effect. It appears to me doubtful whether in this case the orientation which occurs in the bulk of the crystal would be preserved, as is shown by the patterns.

X-ray investigations on benzil have been carried out in an attempt to obtain diffuse maxima. It is doubtful whether positive results could be achieved, since, apart from the considerations outlined above, the structure of the molecule is not sufficiently regular. Any diffuse maxima observed would be correspondingly weak and broad. With anthracene it is possible to obtain diffracted beams in which all atoms of a molecule are in phase. The diffracted intensity is then fourteen times that due to the corresponding number of atoms considered independently. In benzil this ratio is probably not greater than 3 or 4, since it does not appear likely that the atoms of the two benzene groups will all be in phase simultaneously. An approximate calculation gives an estimated band breadth of about three times that to be expected from anthracene.

To attempt to investigate the diffuse-band phenomena with monochromatic X rays, one would require a very short wave-length, very long exposures, and a molecule of considerable symmetry (e.g. anthracene, pyrene) suitably oriented.

§2. COMPARISON OF ELECTRON DIFFUSE MAXIMA WITH X-RAY EXTRA SPOTS

Although experimental difficulties have so far prevented direct investigation of the effect of temperature on the diffuse band pattern, it appears that their appearance is, in fact, due to thermal vibrations. If this is the case, one would expect a close relation between the two types of subsidiary maxima present in single-crystal diffraction patterns, both of which should be predictable from a single comprehensive thermal theory. At the moment this theory has not been advanced, due both to the mathematical difficulties involved and to the lack of sufficiently accurate experimental data. We are therefore faced with the difficulty that, to account for these presumably related phenomena, we have to use two different explanations, the one based on vibrations throughout the crystal, the other on a hypothetical independence of phase in the vibrations of adjacent molecules. In what follows, an attempt is made to indicate possible lines along which the two apparently distinct explanations may be reconciled.

An interesting comparison may be drawn in terms of the phase relationship of the neighbouring diffracting elements or groups. Each scattering centre

(e.g. atom) will be taken to have co-ordinates of the form $n_1+x_0+x_1$, $n_2+y_0+y_1$, $n_3+z_0+z_1$ along the three axes measured in terms of the corresponding axial distances a_1, a_2, a_3. n_1, n_2, n_3 are integers defining the unit cell in which the atom is placed, x_0, y_0, z_0 are the additional fractional co-ordinates taken relative to the origin of the corresponding unit cell, and x_1, y_1, z_1 are the additional displacements due to thermal vibrations.

If h, k, l are the Laue numbers for given incident and emergent beams, the amplitude of the wavelet scattered from the atom can be written proportional to

$$f e^{i\omega t} e^{2\pi i \Sigma h(n_1+x_0+x_1)},$$

where the summation extends over the three co-ordinates and Laue indices. The amplitude for the whole crystal is then

$$A \propto e^{i\omega t} \sum_{n_0,\ldots} \{e^{2\pi i \Sigma h n_0} \sum_{x_0,\ldots} [f e^{2\pi i \Sigma h n_1} e^{2\pi i \Sigma h x_1}]\}$$
$$= e^{i\omega t} \sum \{e^{2\pi i \Sigma h n_1} \sum [f e^{2\pi i \Sigma h x_0} (\cos\phi + i \sin\phi)]\},$$

where ϕ is the additional phase-angle introduced by thermal vibration. $\phi = 2\pi i \Sigma h x_1$ and its average value is zero.

To obtain the mean intensity we must multiply A by its conjugate complex and average the resultant intensity over all possible vibrations of the crystal. The same result is achieved by taking all the cross-product terms arising from A and A^*, averaging, and then adding. This inversion of the order of summation and averaging is of course only permissible since we are dealing with a sum.

A typical cross-product term is

$$e^{2\pi i \Sigma h(n_1-n_1')} f f' e^{2\pi i \Sigma h(x_0-x_0')} (\cos\phi \cos\phi' + \sin\phi \sin\phi').$$

It is the average value with respect to time, of the last factor involving ϕ, which decides the effect of the thermal vibrations on the contribution of this cross-product term to the intensity.

An accurate evaluation of $\cos\phi\cos\phi' + \sin\phi\sin\phi'$ or $\cos(\phi-\phi')$ requires considerable information on the interatomic forces in the structure. Certain interesting conclusions can, however, be reached from more general considerations.

We have previously assumed (Charlesby, Finch and Wilman, 1939) that atoms vibrate within the same molecule in phase, but those in different, albeit neighbouring, molecules, are independent. With this approximation $\cos(\phi-\phi')$ has an average value $\overline{\cos\phi}\,\overline{\cos\phi'} + 0$ or $(\overline{\cos\phi})^2$ for cross products involving atoms in different molecules. For atoms within the same molecule, the mean value has the greater value, 1. The expression for the (average) intensity is therefore

$$I \propto \sum_{x_0} \ldots \sum_{x_0}' \ldots e^{2\pi i \Sigma h(n_1-n_1')} f f' e^{2\pi i \Sigma h(x_0-x_0')} (\overline{\cos\phi})^2 + \sum_{1=n_1'} \ldots \sum_{x_0} f f' e^{2\pi i \Sigma h(\ _0-x_0')} \times 1,$$

where the first summation excludes cross products involving the same molecule twice, while the second only includes these. The former restriction can be removed:

$$I \propto \sum_{n_1} \ldots \sum_{x_0} \ldots e^{2\pi i \Sigma h(n_1-n_1')} f f' e^{2\pi i \Sigma h(x_0-x_0')} (\overline{\cos\phi})^2$$
$$+ \sum_{n_1=n_1'} \ldots \sum_{x_0 x_0'} \ldots f f' e^{2\pi i \Sigma h(x_0-x_0')} (1 - \overline{\cos\phi}^2),$$

The latter summation arises of course from the relatively higher contribution of cross products from the same molecule, which are always in phase.

It is implicitly assumed in this argument that all molecules are subject to similar forces, and hence have a similar mean value for $\cos\phi$.

The expression for the intensity can then be readily seen to consist of the usual expression for the spot pattern, but modified by the thermal factor $(\overline{\cos\phi})^2$, and in addition, an expression corresponding to a very limited lattice, extending over one molecule only. The latter is multiplied by the thermal factor $(1-\overline{\cos\phi}^2)$ and the number of terms of this nature, i.e. N.

$$I \propto (A^2+B^2)\,\Pi\,\frac{\sin^2 M_1 nh}{\sin^2 \pi h}\,.(\overline{\cos\phi})^2+N\sum_p(A_p{}^2+B_p{}^2)(1-\overline{\cos\phi}^2),$$

in the case where there is more than one independently vibrating molecule per unit cell.

In a further approximation, it becomes necessary to consider the interaction between the displacement of different vibrating units (e.g. molecules). This may be carried out rigorously by resolution of thermal displacements into normal vibrations throughout the crystal. In more complicated crystals, such as those which give rise to diffuse bands, not all the information required is available. It can, however, be expected that the influence of the displacement of one molecule on its neighbours will be more considerable than that on more distant molecules. Thus ϕ and ϕ' are independent for sufficiently distant molecules, but related in some as yet undefined manner for adjacent molecules.

These two conceptions are in a sense complementary. In the thermal-wave conception, the displacement of any molecule (or a corresponding grouping) is obtained by a summation of the wave amplitudes with arbitrary phase angles. Since these waves form an almost continuous spectrum of frequencies over a wide range, coherence in the phase of the vibrations will only occur between molecules which are sufficiently close, e.g. when the distance apart is of the order of the shortest wave-length present in the vibrational spectrum. Around each vibrating unit we may therefore consider a rather indefinite region outside which thermal vibrations bear no phase relationship to that of the unit considered. Cross-product terms involving it and any outside units will therefore be modified by a thermal factor $\cos(\phi-\phi')$, where ϕ and ϕ' are independent, and whose average value, as above, is therefore $\overline{\cos\phi\cos\phi'}$, i.e. $(\overline{\cos\phi})^2$. On the other hand, cross products involving it and units falling within the region will give rise to different thermal factors $\cos(\phi-\phi')$. In particular, for the cross product of any molecule with itself, this factor has the value unity. The actual evaluation of the intermediate cases of partial dependence would entail methods and knowledge similar to those required in the normal vibration method. It can, however, be assumed in almost all cases that ϕ and ϕ' tend to be of the same sign, i.e. $\overline{\phi\phi'}>0$. In this case we have

$$1 \geqslant \overline{\cos(\phi-\phi')} > (\overline{\cos\phi})^2,$$

or $\overline{\cos(\phi-\phi')}=(\overline{\cos\phi})^2+T^2$, where T^2 generally increases from zero, as the two molecules which give rise to the cross-product term considered are closer.

The expression for the intensity is then obtained by a summation of all the cross-product terms, of which those corresponding to closer molecules are in general of larger amplitude.

$$I \propto (\overline{\cos\phi})^2 \sum_{n_1 \ldots} \sum_{x_0 \ldots} e^{2\pi i \Sigma h(n_1 - n_1')} ff' e^{2\pi i \Sigma h(x_0 - x_0')} + \sum_{n_1 \ldots} \sum_{x_0 \ldots} e^{2\pi i \Sigma h(n_1 - n_1')} ff' e^{2\pi i \Sigma h(x_0 - x_0')} \cdot T^2.$$

The first term gives rise to the usual Laue-spot pattern modified by the thermal factor $(\overline{\cos\phi})^2$, while the second term will be similar in character, but the summation is, in fact, limited to regions of mutual coherence. The diffraction pattern obtained will apparently consist of the superposition of the usual spot pattern and approximately of the pattern obtained from a limited lattice, although the intensity distribution as between the spots will be modified.

It has already been shown (W. H. Bragg, 1941; Preston, 1939) that the extra spots observed in x rays can to a considerable extent be correlated with the existence of hypothetical groups of particles. This is in approximate agreement with the conclusions derived above. The assumption of groups is almost equivalent to taking T^2 as constant over a small region, surrounding each scattering centre, and zero over the remainder of the crystal. Actually it will decrease from the value $1 - \overline{\cos\phi}^2$ to zero in a more continuous fashion. This distinction becomes important when attempts are made to deduce the size of the hypothetical group. The intensity distribution within each diffuse spot will be appreciably different in the two cases.

Moreover, it offers a means of establishing the approximate size of the *regions of coherent vibration*. In the case of certain simple inorganic structures (KCl, Al, etc.) these appear to cover not more than several unit cells in any direction. In the case of Al, Preston (1939) finds that this region extends over the twelve neighbours of any atom.

Returning now to the more complex structure (e.g. organic crystals), it may be expected that these regions will be relatively smaller, due to the larger number of vibrations to be considered, the greater amplitudes of vibration (cf. elastic constants), and the larger mass of each vibrating unit (resulting in slower vibration and increased importance of the higher frequencies). The effective coherent-vibration region may well cover only the unit cell. This, too, is borne out by consideration of the anthracene crystal, where a theory assuming virtual independence in the phase of the vibrations of different molecules leads to very satisfactory conclusions. It should perhaps be pointed out that the normal co-ordinate method, as given in the Faxén-Waller theory, is liable to fail when the amplitudes of vibration become very considerable (as is indicated by the low melting point of these crystals, etc.). The general arguments used above and the conclusions derived from them will not, however, be affected.

§ 3. CONCLUSION

Subject to suitable crystals being obtainable, the molecules of which can behave as diffraction gratings of sufficient extent, it is expected that diffuse band phenomena should be observable in x-ray diffraction. Wide angles of diffraction and short wave-lengths will, however, be required, as well as long

exposures and suitable crystal orientation. Moreover, it is assumed that other effects (e.g. general scattering) do not obliterate the effects which might otherwise be noted.

Extra spots can be considered to arise from the lack of coherence in the thermal vibration of different atoms or molecules of the crystal. The lack of phase relationship between the periodic displacement of distant scattering centres causes a decreased contribution to the scattered intensity. On the other hand, the contributions from neighbouring vibrating atoms or molecules, where this lack of coherence is less marked, will be relatively larger. The total diffracted intensity may thus be considered to consist of two parts, the first arising from the whole crystal, but with a decreased intensity due to thermal agitation. The second part arises from the additional contribution from close neighbours in the structure; this part simulates the pattern obtained from very small groups of molecules, the size of which is determined by the region of coherent vibration, i.e. the region where the relationship between the phases of the vibrations of different atoms is not entirely random. This region appears to extend approximately over several atomic spacings in simple inorganic structures, and over a single unit cell in more complex organic molecular compounds.

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REVIEWS OF BOOKS

The Theory of Rate Processes, by SAMUEL GLASSTONE, KEITH J. LAIDLER and HENRY EYRING. Pp. viii + 611. (New York and London: McGraw-Hill Book Co., Inc., 1941.) 42*s*.

This book has the more explanatory sub-title *The Kinetics of Chemical Reactions, Viscosity, Diffusion and Electro-chemical Phenomena*. It is an account of the method, generally associated with the names of Eyring, Polanyi and others, of the calculation of rates of reaction from the fundamental properties of the reacting species.

Some of the first reactions to be carefully investigated were homogeneous gas reactions which proceeded, in the range accessible to measurement, at rates which could be accounted for quite simply on the basis of a kinetic-theory collision mechanism, assuming that only collisions fulfilling certain energetic requirements led to reaction. Further work led to the discovery of reactions with rates both considerably slower and faster than was predicted by the simple calculation of fruitful collisions. The theory of absolute reaction rates (or the transition-state method), developed later, shifts the emphasis from the collision to the activation mechanism. It is perhaps important to notice here that at the roots of both theories lies the assumption that the equilibrium concentration of "activated complexes" is unaffected by the progress of the reaction. The authors state this explicitly (p. 185), but they do not mention that there are certain reactions of very low activation energy, e.g. the quenching of the fluorescence of dissolved hydrocarbons by oxygen, and possibly certain chain reactions, where the assumption almost certainly does not hold.

The rates of many reactions may be expressed in the familiar form, rate $= A \cdot e^{-E/RT}$, where A is a frequency factor and E is an energy of activation. The application of quantum mechanics to the evaluation of the energy of activation was first considered by London in 1928. His suggestion that a single function should be capable of representing the state of an electron throughout chemical reaction led to the derivation of an approximate equation giving the potential energy of a system with variation in the internuclear distances. The exact solution of this equation, even for the simplest cases, is exceedingly difficult, but by making further approximations—mainly regarding the distribution of energy between coulombic and exchange terms—Eyring and Polyani developed what has become known as the "semi-empirical method" for calculating activation energies. Their argument makes use of the concept of the energy barrier: considering the simple reaction, A + B = AB* = products, if the potential energy of the system is plotted as a function of an internuclear distance co-ordinate, a humped curve is obtained in which the maximum corresponds to the potential energy of the activated complex AB*, the activation energy being given by the height of this maximum over the point corresponding to the system A + B at infinite separation. To determine the rate of the reaction, it is then only necessary to evaluate the frequency with which molecules pass over the barrier. It is an important result of the transition-state theory that it is able to identify this frequency with the product of a universal frequency, kT/h, and an equilibrium constant, expressed in terms of partition functions, so that A, the frequency factor, is identified with $\left(\frac{kT}{h}\right)\frac{F_*}{F_A F_B}$, F_*, F_A and F_B being the partition functions of the activated complex and of the reactants A and B respectively. (In practice, a constant, κ, unity or less, the *transmission coefficient*, dependent on the detailed shape of the potential energy contours in the neighbourhood of the activated state, has also to be introduced into this expression.)

The relation giving the rate of reaction may now be written :

$$\text{rate} = \kappa \left(\frac{kT}{h}\right) \frac{F_*}{F_A F_B} e^{-E_0/RT},$$

whence it can be shown that

$$\text{rate} = \kappa \left(\frac{kT}{h}\right) e^{-\Delta F_*/RT} = \kappa \left(\frac{kT}{h}\right) e^{-\Delta H_*/RT} e^{\Delta S_*/R},$$

where ΔF_*, ΔH_* and ΔS_* are the free energy, heat and entropy changes accompanying the activation process : here ΔH_* differs only slightly from the experimental activation energy. It is by no means an inconsiderable virtue of this treatment that emphasis is thus laid on the free energy, rather than on the heat, of activation. The rather general form of these expressions for the rate of passage over an energy barrier accounts for the possibility of the interesting applications of the theory noted in the sub-title of the book.

The book divides into two parts. Pp. 1 to 201 contain a rather academic introduction, and in Chapters II to IV, entitled *Quantum Mechanics*, *Potential Energy Surfaces* and *Statistical Treatment of Reaction Rates*, respectively, are derived the results to be used in the later application of the theory. The first part, therefore, is an exposition of the method outlined above : perhaps the main criticism is that Chapter II, a very concentrated discussion of the results of quantum mechanics required for the subsequent treatment, appears to fall between two stools in being too terse for the more general reader, while redundant for the student familiar with the subject. This criticism may be outweighed by the advantage of having a development of the subject in the form required by the authors for their present purpose.

In the succeeding pages (pp. 202 to 599) are discussed the applications of the theory : the headings are *Homogeneous Gas Reactions*, *Reactions involving Excited Electronic States*, *Heterogeneous Processes*, *Reactions in Solution*, *Viscosity and Diffusion* and *Electrochemical Processes* (Chapters V to X). Most of the material has already appeared in the literature (although some has so far only been published in rather inaccessible theses), but the attempt at a connected story—even if the story is at present incomplete—is successful, and the result highly stimulating. The applications discussed in the first four of these chapters have provided the considerable experimental justification for the essential correctness of the theory, and its impetus to experimental work is made clear in these pages. An interesting example is the $H—CH_4$ complex, which calculation shows to possess a fair measure af stability.

The chapter on viscosity and diffusion is less satisfactory. The application of transition-state theory to the liquid state, in conjunction with the theory of holes in liquids, does not, at present, appear to be very profitable. The exuberance of the authors, however, carries them on to make statements which are, at the least, highly arbitrary. For example, regarding the variation of viscosity with pressure, curves are given (figure 124, p. 509) of this variation for pentane and for ethyl ether. The calculated curves are obviously diverging more and more from the experimental points with increase of pressure, so that at a pressure of 12×10^3 kg./cm^2 the figures for ethyl ether are 62 millipoise (observed) and 105 millipoise (calculated). It hardly seems possible, therefore, to " predict with fair accuracy the influence of pressure on the viscosity of liquids ".

In the last chapter, *Electrochemical Processes*, an interesting and again stimulating outline is given of the application of the theory to problems of ionic mobility and of electrode phenomena.

The printing and lay-out of the book are excellent, and it is remarkably free from serious misprints. A few minor errors have been introduced into the references, but they are not of sufficient importance to be noted here. In figure 108 (p. 429) the

error in the legend to the original diagram of Livingstone has been perpetuated: reaction IV should be "$CH_3CO_2C_2H_5 + OH^-$". The subject index is not very complete, and it is possible that a separate index of reactions would make for greater ease in using the book. The system of referencing used, that of numbered footnotes, is rather inconvenient when the reader, as sometimes happens, is referred to a footnote number which may be a score of pages back. It would have been better if the references had been collected at the ends of each chapter. These are small things, but they would have increased the usefulness of a book certain to be widely read. For, in spite of lack of self-criticism and the rather biassed outlook of this book, its readers will be grateful to the authors for a highly interesting account of a theory which seems likely to make many further important contributions to the study of physico-chemical phenomena.

R. F. B.

Practical Acoustics and Planning against Noise, by HOPE BAGENAL. (London: Methuen and Co., 1942.) Price 7*s.* 6*d.*

The appearance of a book concerned in the main with post-war development causes elation in some, exasperation in others. Certain it is that in the topsy-turvy world which war brings in its train, scientists who have, directly or indirectly, served on committees for the abatement of nuisances like smoke and noise are now asked to exercise their wits to produce as much smoke or noise as possible. It is, accordingly, in the light of what we hope a post-war world may look like, that this little volume must be reviewed.

In effect, it is a smaller version of the book which Mr. Bagenal and Dr. Alexander Wood wrote some years ago, with most of the citations and calculations omitted. Added to this, that Mr. Bagenal has brought it up to date, notably in regard to later experience in broadcasting studio and theatre design, and we find a book more suitable in size and scope for the student-architect than the practitioner for whom the first was mainly intended. There is, in addition, more emphasis on the reduction of and insulation against noise in this than in the earlier book. Nearly half the book is concerned with what one might call (by analogy with the corresponding divisions in ballistic science) "external acoustics", and rather more than half with "internal acoustics". Actually it is the latter which is the prime concern of the architect, the former being the domain of the sociologist and the engineer.

The author, in the latter portion of the book, gives useful information on suitable designs for various types of buildings. His remarks on the difficult acoustic problems met in designing a church are particularly worth noting.

The physicist may occasionally be shocked by what he will feel are unorthodox uses of familiar technical terms, but since this book is meant for architects he has really no right to complain as long as the author defines the interpretation which he attaches to such words.

E. G. R.

Tables of Squares of all numbers less than 300. 1 page on card. (London: Scientific Computing Service, Ltd., 1942.) 1*s.*